Aalto University
School of Chemical Technology

School of Chemical Technology
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APPLYING EXERGETIC LIFE CYCLE ASSESSMENT FOR EVALUATING THE EFFICIENCY OF METALLURGICAL PROCESSES, CASE: Copper Smelting

Master's Thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 18 March 2013.

Supervisor : **Professor Jukka Koskinen**

Instructor : **Professor Markus Reuter**

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School of Chemical Technology

School of Chemical Technology **Abstract of Master's Thesis**

Degree Programme of Chemical Technology

Author

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Title of Thesis

APPLYING EXERGETIC LIFE CYCLE ANALYSIS FOR EVALUATING THE EFFICIENCY OF METALLURGICAL PROCESSES, CASE: Copper Smelting

Abstract

This thesis tested and debugged the software link between the the HSC-Sim ™ and environmental software GaBi while enhancing the HSC-Sim ™ with an exergetic calculation functionality for flow sheets. Copper metallurgy was used as a test example to check the software compatibility and calculations. While various data are presented as a result of the simulations, the main focus of this thesis was rather on the development of HSC-Sim™ functionality and further developments are required in order to be able to make definitive statements on coppermaking technologies.

The literature part of Thesis reviewed the footprinting, the concept and scope of Life Cycle Assessment (LCA) were generally described and its current problems were presented. In connection to these exergy was introduced. The motivation for connecting exergy to LCA was expressed and the findings of articles connecting exergy to LCA were summarized. The life cycle of copper was introduced including the alternative process steps of Copper production from ore to high grade metal. Similarly the principle chemical reactions and description of compositions in these steps were introduced as a reference for simulations. Finally the simulation programs used for analyzing processes were presented in general.

The Experimental part of Thesis consists of simulation of two different Copper production process's including Flash Smelting with Peirce-Smith Converter and Flash Smelting with Flash Converter using Outotec's HSC-Sim ™ software linked together with PE International's GABI software to perform Life Cycle Assesment (LCA). An Exergetic Life Cycle Assesment (ELCA) was demonstrated using the HSC-Sim ™. In order to do this the exergy calculation methods of HSC were revised and corrected accordingly and debugging for LCA tool of the HSC-Sim ™ was done.

The novelty of Thesis was a demonstration of in-depth LCA and ELCA of different copper production processes by using simulation tools and proper process data as compared to traditional LCA's that are based typically on average values giving a significant source for inaccuracy for results on specific processes. This gives the possibility to better understand the weak points of processes and to find ways to improve the processes to more thermodynamically efficient and environmentally friendly level.

The results of this Thesis suggest that the link between the programs is working and the tools are adequate for performing proper assessment. The HSC-Sim™ proved also its compatibility for performing an ELCA. When the models are considered, as the fugitive emissions and acid plants are not fully included within the models, no statement regarding the technology could be made. None the less it was possible to conclude that the units where most exergy efficiency improvement seems to exist are those with greatest temperature differences from the reference temperature such as the hot slag and anode copper as well as the matte granulation.

Numerous suggestions on exergy calculations on HSC-Sim ™ have been made, especially on mixing exergies. These suggestions have been summarized in appendix Q with sample calculation on non-ideal mixing. All the data and results can be found in accompanying memory stick.

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Kemian tekniikan korkeakoulu **Diplomityön tiivistelmä**

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Tekijä

Karri Matias Lehtonen

Diplomityön nimi

EXERGEETTISEN ELINKAARIANALYYSIN SOVELTAMINEN METALLURGISEN PROSESSIN TEHOKKUUDEN ARVIOIMISEKSI, CASE: Kuparin valmistus

Tiivistelmä

Diplomityön tarkoituksena oli HSC-Sim ™ simulointiohjelman ja elinkaarilaskentaohjelma GaBi:n välisen yhteensopivuuden testaaminen ja virheiden etsintä, ja toisaalta HSC-Sim ™ ohjelman exergialaskennan tarkastaminen ja kehittäminen prosessikaavioita hyödyntäen. Kuparin valmistusta käytettiin testauksessa esimerkkinä yhteensopivuuden testaamisessa ja exergialaskennassa. Vaikka simuloinnin tuloksia on esitelty laajalti, pääaiheena oli kuitenkin HSC-Sim ™ ohjelman toiminnallisuuksien testaaminen ja eräitä lisätutkimuksia vaaditaan kupariteknologioiden arvioimiseksi.

Diplomityön kirjallisuusosuus esittelee tuotantoon liittyviä jalanjälkilaskentaan kytköksissä olevia metodeja kuten elinkaarianalyysin (LCA) konseptin, jonka laajuus ja tämän hetkiset heikkoudet käydään läpi. LCA:n heikkouksien korjaamiseksi exergian käsite tehdään tutuksi. Exergian ja LCA:n yhdistämisen edut tehdään selviksi. Exergian ja LCA:n yhdistämiseen liittyvien artikkeleiden löydökset esitellään. Kuparin elinkaari käydään läpi ja vaihtoehtoiset prosessivaihtoehdot kuparimalmista metalliseksi kupariksi esitellään samalla. Kuparinvalmistukseen liittyvät tärkeimmät kemialliset reaktiot esitellään. Lopulta esitellään käytetyt simulointiohjelmat.

Työn kokeellinen osuus koostuu Outotec Oyj:n kehittämien kuparin liekkisulatusprosessien, liekkisulatus-liekkikonvertoinnin ja liekkisulatus-Peirce-Smith-konvertoinnin, simuloinnista ja analysoinnista käyttäen apuna Outotecin kaupallista HSC-Sim ™ prosessisimulointiohjelmaa yhdessä PE-International ltd:n LCA-ohjelman GaBi:n kanssa. Ohjelmia apuna käyttäen suoritettiin elinkaarianalyysi ja tämän lisäksi myös tehtiin exergeettinen elinkaarianalyysi. HSC-Sim ™ in exergian laskennan virheitä korjattiin ja LCA työkalun käytössä ilmenneitä virheitä korjattiin. Saatujen tulosten perusteella prosessin termodynaamisen tehokkuuden parantamisen ongelmakohdat pyrittiin tunnistamaan.

Työn uutuus on poikkeuksellisen yksityiskohtaisen kuparin valmistusprosessin elinkaarianalyysin mahdollistuminen simulointityökalujen linkittämisen kautta, joka mahdollistaa tavanomaista keskiarvoihin perustuvaa elinkaarianalyysimenetelmää huomattavasti yksityiskohtaisemman analyysin tekemisen. Aiempaa suurempi yksityiskohtaisuus ja exergialaskennan mukaan tuominen analyysiin antaa myös mahdollisuuden tunnistaa prosessin termodynamiikan kannalta ongelmallisimmat kohdat aiempaa tarkemmin.

Diplomityön tulokset osoittavat, että ohjelmien yhdistämisestä saatavat edut LCA:n tekemisessä on realisoitavissa. HSC-Sim™ osoittautui myös oivalliseksi työkaluksi ELCA:n suorittamiseksi. Demonstraatio kuparinvalmistusprosessilla osoittaa, että entistä tarkempi analyysi on mahdollista, jos prosessimalleihin sisällytetään vielä karanneet päästöt, jotka liittyvät Peirce-Smith prosessiin, ja toisaalta happotehtaaseen liittyvät mahdolliset exergiatappiot. Täsmällistä vertailua kuparinvalmistusprosessimallien välillä ei voitu kuitenkaan suorittaa edellisistä puutteista johtuen. Alustavien tulosten perusteella merkittäviä mahdollisuuksia exergiatehokkuuden parantamiseksi löydettiin erityisesti suurien lämpötilaerojen, erityisesti kuuman kuonan, anodikuparin lämmön ja pelletöinnissä kuparikiven lämmön hyödyntämisessä.

Useita ehdotuksia HSC-Sim ™:in exergialaskennan tarkkuuden parantamiseksi tehtiin liitteessä Q, erityisesti sekoittumisen exergialle. Liitteestä löytyy myös esimerkki epäideaalin seoksen exergian laskemiseksi HSC-Sim ™:issä. Kaikki data ja esimerkit löytyvät ohessa olevalta muistitikulta.

Professuurin nimi **Tehdassuunnittelu**	**Professuurin koodi** **KE-107.**
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FOREWORDS

I would thank my Instructor, Professor Markus A. Reuter from Outotec Oyj, for his opinions and advices on the contents of this Thesis and for pushing me on when it was needed. He also established the connections between HSC-Sim ™ -models in GaBi and gave me the LCA data that was based on the models that I had provided for him. We did have some nice discussions about the ethics of food production, too. I would like to thank Professor Jukka Koskinen for discussions on exergy and helping me to understand some of the issues that I had thought previously.

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own good. Also Mikael Jafs, Markku Lahtinen, Akusti Jaatinen, and Peter Björklund and Pyry from Outotec deserve thanks for providing me information concerning consumption of resources external to the processes itself.

I would like to thank my parents Antti and Kristiina for giving me life and good home education that has been supporting for my efforts to understand and explore the world and my dear sisters Kiira and Marleena for support and kindness through my life. As well I'd like to thank them for their efforts for being my personal stylists. Additionally I'd like to thank my partner Eerika Siponen for her patience and believing on my capabilities. It has been most useful when I've lacked the belief on myself a few times during the course.

I would thank the world for being such a great place to live (for now).

Espoo, Finland, 31.1.2013

Karri Lehtonen

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Nomenclature

Symbol	Explanation	Unit
B	Exergy	J
B_{PH}	Physical exergy	J
B_{CH}	Chemical exergy	J
B_P	Potential exergy	J

B_K	Kinetic Exergy	J
H	Enthalpy	J
S	Entropy	$\frac{J}{K}$
T_0	Temperature of reference environment	K
x_i	Mole fraction of ith component	-
μ_{i}	Chemical potential of species i at T, p, c	$\frac{J}{mol}$
$\mu_{i,0}$	Chemical potential of species I at T_0, p_0, c_0	$\frac{J}{mol}$
R	Gas constant	8.314 $\frac{J}{molK}$
p_i	Patrial pressure of substance at T, p	bar
$p_{i,0}$	Partial pressure of substance at T_0, p_0	bar
$\Delta_f G^0$	Gibbs free energy of formation	$\frac{kJ}{mol}$
n_{el}	Moles of element in 1 mol of substance	mol
$B^0_{CH,el}$	Chemical exergy of element	kJ
$B_{CH,mix}$	Chemical exergy of mixing	kJ
$B^0_{CH,i}$	St. chemical exergy of ith component	kJ
γ_i	Activity coefficient of ith component	-
W_i	Work index	$\frac{kWh}{t}$
P_{80}	80% of product smaller than this	μm
F_{80}	80% of feed smaller than this	μm
B_{in}	Exergy of inputs	J
$B_{product}$	Exergy of product	J
B_{waste}	Exergy of non-product	J
$\Delta B_{process}$	Internal exergy loss of the process	J
B_{out}	Exergy of outputs	J
B_{lost}	Total exergy lost in the process	J
U	heat transfer coefficient	W/m^{2}K

Q	heat flow	W
A	heat transfer area	m^2
ΔT	logarithmic temperature difference	K

1 Introduction

The goal of this thesis is to examine the possibility to improve the Life Cycle Assessment (LCA) of a process in various ways. The main objective for succeeding in this was to test and debug the connectivity between the simulation program HSC-Sim ™ and LCA program GaBi. Generally the LCA programs use average data in the assessment but as the real processes are exact, the variations from the average can't be properly assessed using the average values. Also another problem is that the depletion of natural resources is not included to the LCA and for this reason the Exergetic Life Cycle Assessment (ELCA) is required as the exergy gives information on this (R.L. Cornelissen, 1998). These are main areas of improvement in LCA.

The benefits of connecting HSC-Sim ™ and GaBi in order to perform a LCA are best described in the Figure 1. This connection enables us to gain access to highly detailed process information regarding the environmental impacts.

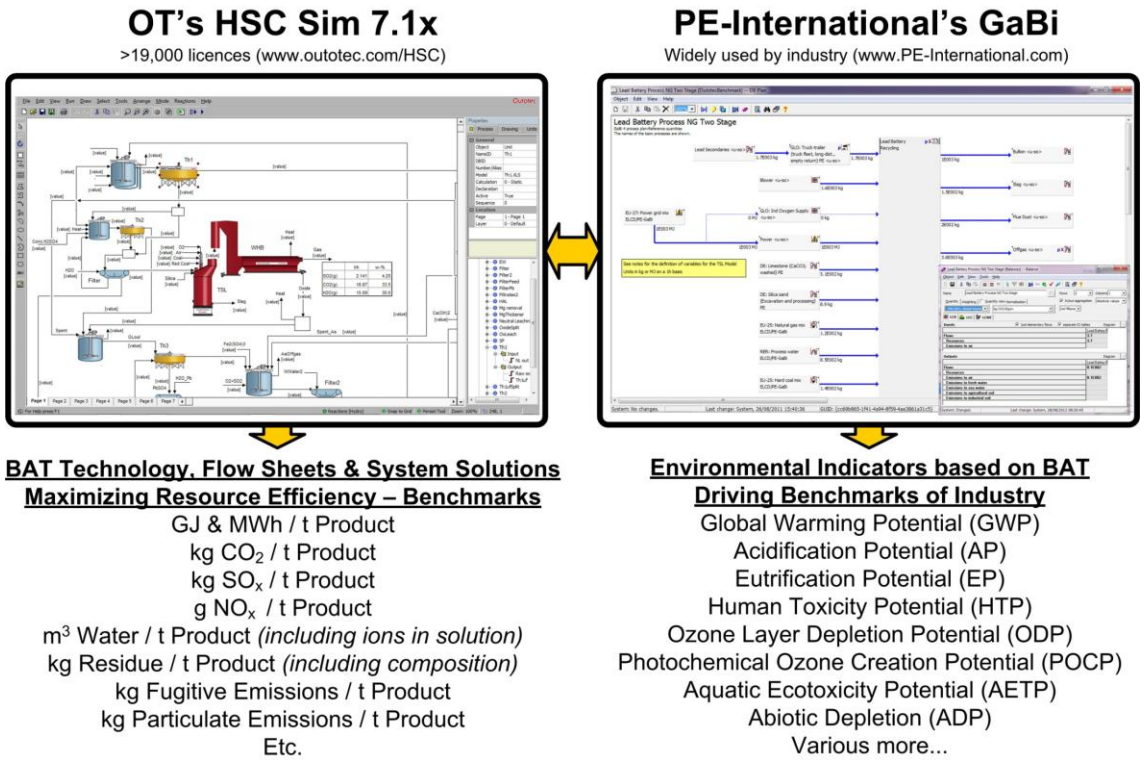


Figure 1, Connecting HSC-Sim ™ 7.1 and GaBi (obtained from M.A Reuter)

1.1 Purpose and Novelty

Currently the exergy analysis as well as LCA of copper production has been constrained to rough macro level production or recycling analysis (see for example Gößling-Reisemann, 2006[1], 2008[2], R.U. Ayres et al., 2002, 2006b, M.B.G. Castro et al. 2007) but more specific micro level process specific information is required to better understand the production system. The question of plant location, technology and ore feed contents effects on environmental performance was first raised by Castro et al. (2001) in broader context as they analyzed environmental performance of two technologies in copper production plants located in Australia and Chile. Meanwhile the means to perform more specific analysis easily has been missing. One purpose of the Thesis is to demonstrate on how to perform such an analysis with adequate tools.

Besides that this detailed micro level Exergetic life cycle analysis of Copper process has not been done yet, though somewhat detailed entropy analysis of pyrometallurgical processes has been made (S. Gößling-Reisemann, 2006, 2008). Since the production plant features and processing methods vary according to the ore grade and content it has been difficult to analyze the efficiencies of separate production plants. The interest then lays on the impacts and the exergy of different processes to better understand the overall effects of copper refining on more detailed level in terms of efficiency and resource use. Detailed, plant specific, computer aided exergy analysis together with LCA is a tool that enables the identification of the most significant waste streams, exergy losses and potentials for environmental and process improvements.

The main focus of this Thesis was to demonstrate the possibilities of HSC 7.1, GABI and HSC-Sim ™ programs in performing LCA and exergy calculations of the Copper processes. As a demonstration of using detailed data for LCA example assessments are made for two copper production processes models (Flash Smelter Furnace with Peirce-Smith Converter and Flash Smelting Furnace with Flash Converter Furnace) that are based on real data. The process models consists of Beneficiation, Flash Smelting Furnace related operations and

[1,4] these were actually entropy analysis's of copper production, thus not comparable as such but the results should be similar, see Appendix 9 for the comparable results of S. Gößling-Reisemann (2008)

Electrorefining. In this process the LCA add-in was debugged. The necessary process data and models were be provided by Outotec Oyj.

After the inventory analysis part an ELCA was performed. In relation to this the exergy calculation scheme of HSC-Sim ™ was checked, corrected and improved. The ELCA provided information about the exergetic efficiency of the process and process units. The generalized results from ELCA suggested that an improvement potential existed in the process units where large temperature differences took place, mainly in Flash Smelting Furnace related operations. Also the proper use of landfill could offer opportunities for exergy efficiency improvement. As the data was incomplete regarding the acid plant and fugitive emissions, the results of the LCA as well as ELCA were incomplete and no definitive conclusions on technology could be made.

The demonstration was successful in that it proved that it is possible to archive more detailed LCA by combining the exact process data with environmental data. Besides this the connection between the programs was proved functional and the ELCA was rather easily performable by using the process data as the exergy calculation scheme automated the calculation process.

1.2 Contents

In the first Chapter the copper use in society is taken under observation, the methods of life cycle assessment and exergetic lifecycle assessment are defined, the copper extraction, beneficiation and processing are introduced and main technologies are represented. The main simulation programs are shortly presented.

In the second Chapter the environmental impacts and their significance for improving the processes are presented. The concepts represented in first Chapter are Life Cycle Assessment, Exergy calculations, Exergy analysis and their combination to perform an Exergetic Life Cycle Assessment.

In the third Chapter the coppers life cycle is presented. The scope of copper life cycle is defined including mining and extraction of copper ore, pyrometallurgical processing and the alternative of hydrometallurgical processing. The significance of utilities of these processes are discussed. Also the principles of copper recycling are introduced. The principle processes are discussed shortly for each topic. If the copper processes and copper anthropogenic use are familiar for the reader this Chapter could be ignored.

In the fourth Chapter simulations are highlighted. The basic simulation tools (HSC-Sim ™, HSC 7.0 and GABI) are introduced. Also the experimental part of the Thesis is represented. Finally the two processes that are being simulated and analyzed are discussed. The process flow charts are represented and assumptions required for the simulations are made.

In the fifth Chapter the preliminary results from LCA, exergy analysis and Exergetic Life Cycle Assessment (ELCA) are represented as the model limitations didn't allow full assessment. In this context possible weak points of the models and methods are identified and discussed. The most significant assumptions and restrictions of the models are collected. Most significant limitations are due to the incomplete data on fugitive emissions and the sulphuric acid plant.

In the sixth Chapter preliminary LCA and exergy analysis are performed for the models in order to examine the compatibility of the methods used.

In the summary the purpose, contents and preliminary results as well as the conclusions of the Thesis are once more revised. The LCA add-in of HSC-Sim ™ was found a convenient tool for performing the ELCA and the connection to Gabi was considered as adequate tool for performing more exact LCA.

2 Concepts

2.1 Copper in Society

Copper is the most used non-ferrous metal with a consumption of 22 Mt/a end-use products. Major part of this copper production is used in electronics, wires and cables while it is also widely used in construction for plumbing, taps, valves and fittings, in industry and transport in radiators and heat exchangers and alloys of copper such as bronze are used in marine industry for their good corrosion resistance. (ICSG, 2010).

The refining of copper requires large amounts of energy: some estimates of 45 GJ/t for ore and 20 GJ/t for secondary copper production have been made (A. Lossin, 2012). The main source of environmental impacts of copper Life Cycle comes thus from the production of copper where the mining and minerals processing uses large amounts of energy while smelting and refining account for lesser, though none the less, significant part of the energy consumption (T. Norgate and S. Jahanshahi, 2006, R.U. Ayres, 2002). The embodied energy of mining and mineral processing account for 60% of energy need for copper ore grades of 3% and 90% for copper ore grades of 0,5% while smelting and refining account for the rest 40% and 10% accordingly (T. Norgate and S. Jahanshahi,2006). The energy consumption and costs of copper processing increases significantly as the ore deposit grades are decreasing since grinding and ore handling are highly energy consuming, thus the importance of recovering as much as possible of the copper attached to the ore in refining should have a great significance for the energy consumption of the mining process as it potentially also improves the efficiency of mining (and thus reduces energy consumption/unit of Cu and lowers depletion rate). Also the new innovations could possibly decrease the current technology constrained mineralogical barrier making more of the deposits available. This is likely to require improvements in extraction, smelting and refining technologies.

Smelting and refining are currently considered energy efficient as the flash smelting uses the heat from oxidation reaction of sulphides to smelt the metal reducing the need for external fuels required to keep the process flows molten. The off-gases from furnaces contains significant amounts of heat which is recovered in waste heat boilers Besides this some of the reaction heats are captured when SO_2 that is oxidized first to SO_3 which is further absorbed to H_2SO_4. The heat is further used in drying of the concentrate from froth flotation, preheating

the furnace air/O_2/N_2 inflow or heating the electrolyte solutions to more appropriate temperatures (G.W. Davenport, 2011).

Besides this an energy saving alternative for virgin ore extraction comes from copper recycling. By increasing the recycling efficiency it is possible to lower the need for virgin ores (R.U. Ayres, 2002). Recycling is considered to consist of three different sources of scrap: home scrap (produced and recycled simultaneously within production), new scrap (generated during manufacturing), old scrap (from used products). The two first ones can be reprocessed easily with some cost. The main challenge comes from the old scrap that could be divided to four or five main categories (see for categorizations at ISRI, 1990, Biswas and Davenport, 1994, or Davenport 2010). When it comes to copper, the uses of copper are varied as mentioned before. This not only gives a wide diversification of grades but also a great geographical diversion which makes the recycling costly and energy consuming which are connected to transporting and reprocessing of the scrap. As Giurco et al. (2006) has shown the greatest danger for environment is caused by the low grade scrap which is also the most difficult to reprocess and the findings of Castro et al. (2007) confirm that the exergetic losses (which will be discussed later) of recycling are also significant for this kind of scrap. The main source of low grade scrap is electronics and other consumer products while the bulk of copper is used in wires which can be collected and recycled easily. The wires as well as plumbing and roofs have often very long life time giving the copper products on average around 30-40 years in use (see for example Arpaci and Vendura, 1992 or USEPA, 1983) while the recovery efficiency is estimated to be somewhere between 30-80% depending on the source and country (Sibley et al. 1995, Arpaci and Vendura, 1992). Given the high increase in copper consumption during those years the copper recycling rate is significantly low at around 15-30% (Simada et al., 1999, Edelstein, 1999). Recycling rate is expected to rise as more of this “hidden” copper becomes available in the future. The growth of recycling rate is due to two main reasons: the depletion of high grade deposits will lead to more costly extraction processes and the stall in copper mining volume that will allow higher recycling rate than previously. On the other hand efficient copper recovery from the ore today and increased recycling level of copper scrap could delay somewhat the need to convert to lower grades of copper in the future providing more time for possible technological brake through for less energy consuming technologies. Besides this efficient recovery and recycling should have two significant environmental impacts: it decreases the accumulation of wasted land masses (connected to the mining) and the need to

use energy to mine, transport and process these land masses is decreased. In order to estimate the effects of refining more properly the method of Life Cycle Analysis (LCA) needs to be presented.

2.2 Life Cycle Assessment

A Life Cycle Assessment (LCA) is a standardized method (ISO 14040) that is nowadays increasingly used for estimating the impacts of a process or a system and it is considered in many companies as a core element of environmental policy. It can be defined as "compilation and evaluation of the inputs and outputs and the potential environmental impacts of a product system throughout its life cycle" (ISO 14040, 2006a and 2006b). In practice LCA involves the collection and evaluation of quantitative data from the inputs and outputs of material, energy and waste flows associated with a product over its entire life cycle so that the environmental impacts can be determined (Royal Society of Chemistry (RSC, 2012). Thus the scope of the study needs to be defined; resource stocks and inputs needs to be quantified and their environmental impacts identified and the results interpreted (RSC, 2012). LCA gives numerical values for resource consumption and production of different categories of materials but since "you can't compare apples and oranges" the results may be difficult to interpret as such. For this reason the LCA results need to be weighted to get values for example for the acidification potential (AP) or the Global Warming Potential (GWP) which are based on scientific experimentation and correlations which might include some misinterpretation[3]s. Besides this, LCA doesn't include an evaluation of depletion of the resources, only their consumption. The LCA reveals differences between products and processes but it says nothing on the efficiency of the process (R.L. Cornelissen, 1998).

2.3 Exergetic Life Cycle Assessment

Since Life Cycle Assessment has its flaws as such the concept of exergy analysis needs to be added to LCA to perform Exergetic Life Cycle Assessment (or analysis, ELCA) (R.L. Cornelissen, 1998). This is because by using exergy it is possible to quantify the depletion and consumption of natural resources more accurately (R.L. Cornelissen and G.G. Hirs, 2002). An exergy is a thermodynamic variable that is derived from the first and second laws of thermodynamics (i.e. conversion of energy and decrease in the order of system) and it describes the energy that is available for work "…as a measure of distance from thermodynamic equilibrium…" (R.U. Ayres

[3] For developments in LCA see Guinee et al. 2011.

et al., 1996). The purpose of exergy analysis is to identify the processes that are consuming most of the exergy. By performing ELCA of a process it is possible to get detailed information on process exergy use and identify points where there is most potential for improvement in thermodynamic efficiency. (R.L. Cornelisse, 1998, R.U. Ayres, 2002)

2.4 Copper Mining and Extraction

Copper (element no. 29, M(Cu) 63.546g/mol) is one of the earliest elemental discoveries of human kind being the 23rd most common element in the earth's crust which has become one of the most used non-ferrous metal of this day (A. Lossin 2012, R.U. Ayres et al., 2002)

It is generally used, for its good conductivity of heat and electricity, in electricity carrying, e.g. as in copper wires, which makes about 40-60% of worlds copper consumption (depending on the source), 13% is used in industrial machinery such as heat exchangers, valves, pumps etc. for various reasons and about equal proportion is used for consumer products and electronic equipments, 5% goes to roofs and plumbing for coppers good corrosion resistance, and about 5%-30% of Copper use comes from alloys such as brass and bronze. (ICSG, 2010, T.J. Brown et al., BGS, 2010, A. Lossin, Ullman's Encyclopedia, 2012)

Worlds copper production from primary ore was estimated at 16.2 Mt/a[4] of which Chile, Peru, China and USA contributed about 2/3 of the ore mining while Worlds smelter production was 12.9 Mt and refined copper production was 19.0 Mt/a while old scrap recycling content of whole production was 20-37% accounting for 3.8-7.0 Mt/, depending on source (T.J. Brown et al., 2010, UNEP, 2011[5]). The Worlds accumulated copper-in-use is estimated to be 210.5Mt (J.L.W. Jolly, 1999) but there is some confusion on the scale (see Zeltner et al. 1999). Worlds primary copper reserves were estimated at 310 - 630 Mt not including undiscovered potentially economically feasible reserves that are estimated at least three times this amount and total copper resources of possibly over 3000 Mt (A. Lossin, 2012, D.A. Singer, and W.D. Menzie, 2010, R.U. Ayres, 2002).

Currently economically feasible grades are as low as 0.32% and this feasible grade is expected to decrease as high grade deposits are being mined and the copper prices are expected to rise while currently the mineralogical barrier is considered to be around 0.1% grade beyond which

[4] Mt = Mega tons (metric)
[5] T.E. Graedel et al., 2004, C.R. Risopatron, 2009, ICSG

the extraction will become practically impossible. The typical grades that are being exploited are 0.5-2% although grades as low as 0.3% are utilized in Sweden, while these ores contains significant amounts of gold which makes the mining profitable. (R.U. Ayres et al., 2002, T. Norgate and S. Jahanshahi, 2006, W.G. Davenport, 2011)

2.5 Main Copper Production Processes

There are two process ways for producing copper of which the pyrometallurgical processing is of interest in this Thesis. The process ways are introduced in Figure 2.

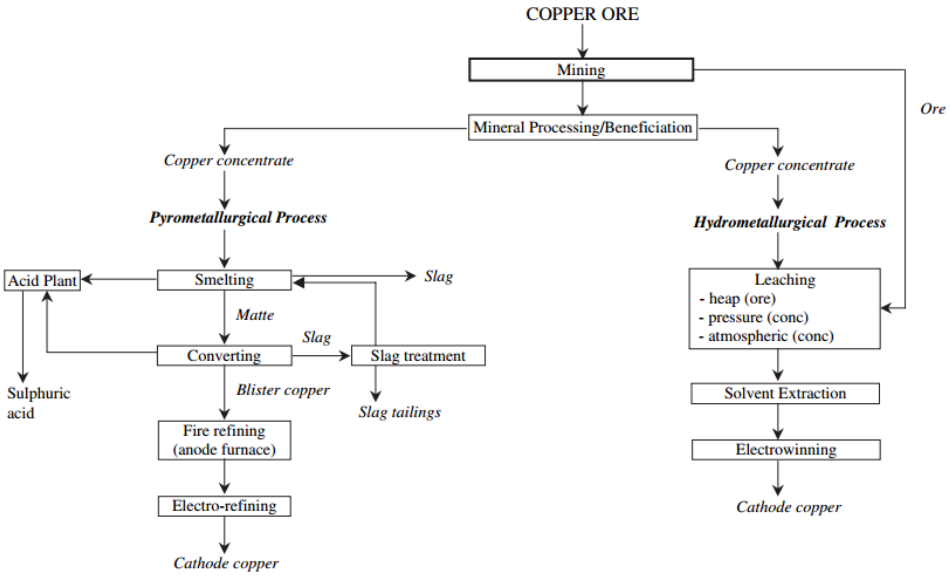


Figure 2, Main processing routes for copper production, (fig. 2, T.E. Norgate et al. 2007)

The first one is **pyrometallurgical process**, which makes up of about 80% of worlds copper production. Sulphide ores containing copper needs to be prepared for pyrometallurgical processing. The copper ores are grinded and concentrated to about 30% Cu concentrate by froth flotation after which most of the water is filtered and dried to lower the moisture down to around 8-10%. The copper concentrate is then smelted with heat from oxidation reaction of Cu-Fe-S concentrate with added SiO_2 flux to produce two separable phases, matte and slag, that are optimized for further treatment and the off-gas has appropriate SO_2 content for sulphuric acid production. The copper is primarily in the matte which has copper concentration of about 55-70% depending on the process. The copper is fed to converters (except for direct-to-copper process) together with flux and oxygen rich air, where further oxidization reaction

occur to produce molten blister copper and iron-silica slag for further processing and off-gas is once more collected for treatment. The resulting molten copper is then cast to plates and resulting anode copper is then electrorefined to high purity copper (99.999%). At this stage it is possible to recover other valuable metals that are found in copper minerals, such as gold, silver and platinum group metals. The dust is recovered from off-gas by using electrostatic precipitation and then recycled or sent for further treatment after which the SO_2 is captured from off gas-by converting it catalytically to SO_3 and then by absorbing SO_3 it to aqueous solution of H_2SO_4. (A. Lossin, 2012, G.W. Davenport, 2011, R.U. Ayres, 2002)

The second process way is **hydrometallurgical processing** (known also as SX/EW-process) where the ores containing copper oxides or the copper oxide rich slags as well as chalcocite ores are (heap) leached with sulphuric acid for longer periods of time. The ore can be crushed and treated with strong H_2SO_4 to improve the process kinetics. The Cu dissolves to aqueous solution of H_2SO_4 directly as is case for oxides or in presence of oxidant and bacteria enzyme catalyst as is case for sulphide minerals such as chalcocite, to form a pregnant solution. The pregnant solution from heap leaching is collected and the copper is extracted using organic extractant which is then stripped with strong H_2SO_4 in separate vessel to create Cu strong electrolyte (40-50 g/l). The electrolyte is then electrowon so that the copper from the electrolyte covers the cathodes at the end. The high purity copper from cathodes is finally mechanically separated and sold to the markets. (G.W. Davenport, 2011, A. Lossin, 2012, R.U. Ayres, 2002, A. R. Burkin, 2001)

2.6 Copper Processing Technologies

The current most significant copper processing technology that makes up over 50% of worlds copper production is Outotec flash smelting technology. Autogenous processes include[6], besides Outotec flash smelting, Inco flash smelting, CIVCET Cyclone smelting*, Contop matte smelting and Flame Cyclone Smelting*. Other pyrometallurgical smelting technologies include: Noranda smelting, Teniente smelting (known also as The Caletones Matte Treatment or CMT), Vanyukov process, Baiyin process, Isasmelt and Ausmelt that use various processes for smelting. Older less significant methods that are mostly used for high grade copper recycling are blast furnace smelting, reverberatory furnace smelting and electric furnace smelting. (G.W. Davenport, 2011, A. Lossin, 2012)

[6] experimental and no more operated technologies are marked with *

The shares of copper smelting capacity can be found in the Figure 2.

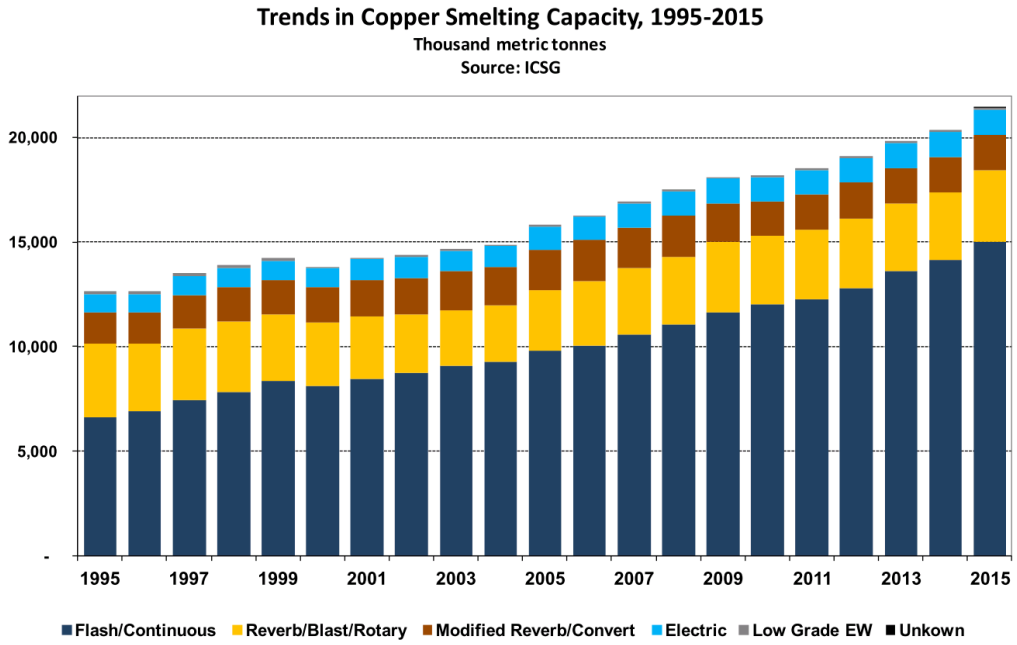


Figure 3, Worlds copper smelting capacity trends, 1995-2015, Source: ICSG (2012)

The most common converter type is Peirce-Smith converter following Hoboken converter, Inspirational converter, Outotec Flash Converter and Top-blown rotary converter (TBRC, mainly used for recycled copper). Peirce-Smith converter can be modified by attaching Air Liquid Shrouded Injector (ALSI) process to it to increase its efficiency and to decrease wearing. (G.W. Davenport, 2011, A. Lossin, 2012)

For increasing energy efficiency and SO_2 capture few continuous pyrometallurgical processes have been developed such as Noranda process*, Mitsubishi process and Kennecott/Outotec Flash Converting Process. Besides these benefits the trend is towards decreasing the capital costs and there exists Direct Blister Smelting (or Direct-to-Copper) processes that doesn't require converting such as Outotec Direct Blister Flash Smelting process and QS process*. The major disadvantage of these processes has been the high copper content in the slag that needs to be recovered increasing the costs. (A. Lossin, 2012)

For hydrometallurgical processing the SX/EW-process is generally used. (A. Lossin, 2012)

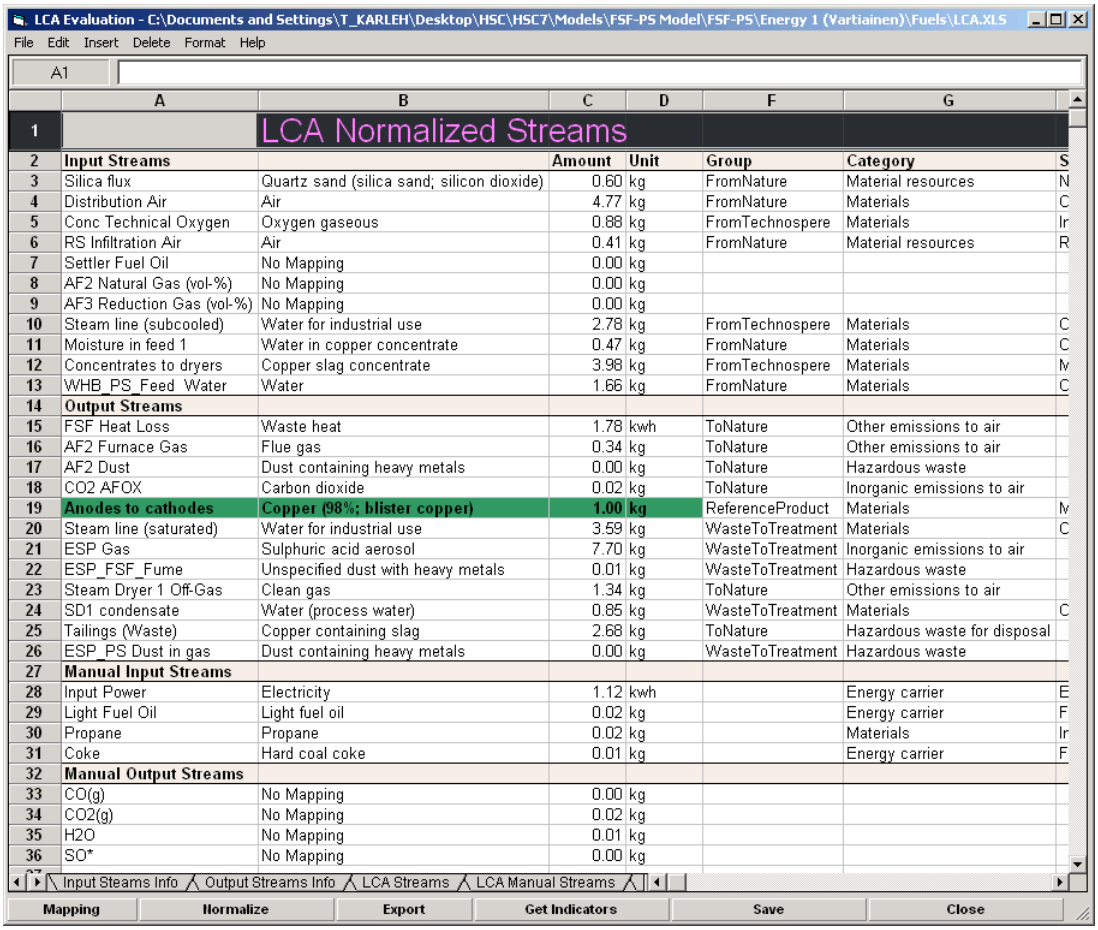
See Chapters 2.5 or 4.3 for descriptions of SX/EW process.

2.7 Simulation

The Thesis uses two programs for analyzing copper production process. The first program used was development version of Outotec's HSC 7.1 ™ and HSC-Sim ™ that contains, in contrast to the public version, exergy calculations and LCA-tool that allows the collection of LCA data directly from the flow sheets and links the HSC-Sim ™ data with PE Internationals LCA program GaBi.

As experimental part of this Thesis the exergy calculation methods of HSC were developed in order to get more accurate results for the exergy calculations. Especially the exergy of mixing was added to the program and the theory is discussed later though the exergy of mixing was added to the HSC-Sim ™ only after this work had been finished and thus the results are commonly not including the mixing exergies besides the floating models where the exergies had to be calculated by hand as HSC-sim ™ lacked this feature for minerals processing mode. Besides this the LCA tool needed some debugging and development ideas which were suggested and discussed in co-ordination with the programmers.

In the LCA-tool it is possible to choose certain key indicators that we might be interested of such as the water consumption and others. The principle of LCA tool is to collect all the data on streams that have no source or destination to a separate sheet. The streams that are collected are then "mapped" in order to group them so that for example the numerous input streams of air might be mapped under the same category. After choosing the main product the LCA-tool allows us to normalize the values for 1 kg of product as shown in the Figure 3.



LCA Evaluation - C:\Documents and Settings\T_KARLEH\Desktop\HSC\HSC7\Models\FSF-PS Model\FSF-PS\Energy 1 (Vartiainen)\Fuels\LCA.XLS

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A1

LCA Normalized Streams

	A	B	C	D	F	G	
2	**Input Streams**		**Amount**	**Unit**	**Group**	**Category**	**S**
3	Silica flux	Quartz sand (silica sand; silicon dioxide)	0.60	kg	FromNature	Material resources	N
4	Distribution Air	Air	4.77	kg	FromNature	Materials	C
5	Conc Technical Oxygen	Oxygen gaseous	0.88	kg	FromTechnospere	Materials	Ir
6	RS Infiltration Air	Air	0.41	kg	FromNature	Material resources	R
7	Settler Fuel Oil	No Mapping	0.00	kg			
8	AF2 Natural Gas (vol-%)	No Mapping	0.00	kg			
9	AF3 Reduction Gas (vol-%)	No Mapping	0.00	kg			
10	Steam line (subcooled)	Water for industrial use	2.78	kg	FromTechnospere	Materials	C
11	Moisture in feed 1	Water in copper concentrate	0.47	kg	FromNature	Materials	C
12	Concentrates to dryers	Copper slag concentrate	3.98	kg	FromTechnospere	Materials	M
13	WHB_PS_Feed Water	Water	1.66	kg	FromNature	Materials	C
14	**Output Streams**						
15	FSF Heat Loss	Waste heat	1.78	kwh	ToNature	Other emissions to air	
16	AF2 Furnace Gas	Flue gas	0.34	kg	ToNature	Other emissions to air	
17	AF2 Dust	Dust containing heavy metals	0.00	kg	ToNature	Hazardous waste	
18	CO2 AFOX	Carbon dioxide	0.02	kg	ToNature	Inorganic emissions to air	
19	**Anodes to cathodes**	**Copper (98%; blister copper)**	**1.00**	**kg**	ReferenceProduct	Materials	M
20	Steam line (saturated)	Water for industrial use	3.59	kg	WasteToTreatment	Materials	C
21	ESP Gas	Sulphuric acid aerosol	7.70	kg	WasteToTreatment	Inorganic emissions to air	
22	ESP_FSF_Fume	Unspecified dust with heavy metals	0.01	kg	WasteToTreatment	Hazardous waste	
23	Steam Dryer 1 Off-Gas	Clean gas	1.34	kg	ToNature	Other emissions to air	
24	SD1 condensate	Water (process water)	0.85	kg	WasteToTreatment	Materials	C
25	Tailings (Waste)	Copper containing slag	2.68	kg	ToNature	Hazardous waste for disposal	
26	ESP_PS Dust in gas	Dust containing heavy metals	0.00	kg	WasteToTreatment	Hazardous waste	
27	**Manual Input Streams**						
28	Input Power	Electricity	1.12	kwh		Energy carrier	E
29	Light Fuel Oil	Light fuel oil	0.02	kg		Energy carrier	F
30	Propane	Propane	0.02	kg		Materials	Ir
31	Coke	Hard coal coke	0.01	kg		Energy carrier	F
32	**Manual Output Streams**						
33	CO(g)	No Mapping	0.00	kg			
34	CO2(g)	No Mapping	0.02	kg			
35	H2O	No Mapping	0.01	kg			
36	SO*	No Mapping	0.00	kg			

Input Steams Info | Output Streams Info | LCA Streams | LCA Manual Streams

Mapping | Normalize | Export | Get Indicators | Save | Close

Figure 4, Normalized streams after mapping in LCA-tool of HSC-Sim ™

The mapping has a double use as it links the HSC streams to PE International's widely used LCA-tool GaBi's database. The linking of streams of separate process models created in HSC-Sim ™ to GaBi database allows model creation for systems in the GaBi environment.

Automated exergy calculations in HSC-Sim ™, on the other hand, allows an identification of the process units where exergy destruction occurs and makes it easy to understand the efficiencies of process in thermodynamic means.

3 Environmental Impacts

In this Chapter the environmental impacts are discussed in general level. The assumptions and limitations of the LCA and ELCA are discussed. The boundaries of the systems are defined for LCA purpose. The exergy is represented and the calculation methods for exergy are shown. The methods for calculating the exergetic efficiencies are discussed. Finally the exergy analysis and the steps for performing the exergetic life cycle assessment are discussed.

3.1 Introduction

In practice all economic activity has some kind of an impact on the environment whether it was direct or indirect. Previously these impacts had been difficult to quantify but new methods were emerged for this purpose from the change of 1990's on as a consequence of grown environmental alarmism.

Most importantly a method called Life Cycle Assessment (LCA) was developed by the International Standardization Organization (ISO) represented in the ISO standards 14040 – 14049 (ISO, 2012). The purpose of LCA is to identify the resource consumption and pollution production of a product or a service over its lifetime from raw materials to disposal and anything in between. The impacts of these substances to the environment are evaluated as part of Life Cycle Impact Assessment (LCIA). LCA is very useful tool when identifying the substances involved with the production and the consumption but it has few weaknesses: all the substances and their environmental impacts needs to be evaluated in some way. This can be problematic as the environmental impacts of a substance are not necessarily known very exactly. Another problem is that LCA does not take into account the scarcity of non-renewable resources. (J.C. Bare, 2010, D.W. Pennington et al., 2004a and 2004b, R.L. Cornelissen and G.G. Hirs, 2002,)

As a consequence a new method that has its basis in LCA called Exergetic Life Cycle Assessment (ELCA) has surged to better answer some of these questions (R.L. Cornelissen, 1998). Exergy is a thermodynamic state property which can be defined as the available work obtainable from the system when it is brought to equilibrium with the environment (J. Szargut, 1988). Exergy connects conveniently physical world resource consumption to the first and second laws of thermodynamics that is the conservation of energy and irreversibility of processes. The principles of ELCA were first introduced by R.L Cornelissen (1998). ECLA uses

the exergy analysis methods developed by various authors[7] most notably J. Szargut (1988, 2005). The purpose of ECLA is to identify the sources of exergy losses, that is, the parts of a process that consumes most resources and energy in thermodynamic means. Besides this the ELCA can be used to estimate the harmfulness of emissions to the nature as exergy is by definition the maximum work obtainable from the system so as the exergy value of an emission is large so is its potential to do (harmful) work towards nature. In this sense it can be regarded as a single number indicator for the harmfulness of the process as total.

Basically all the methods presented here can be regarded as part of Environmental Impact Assessment (EIA) as represented by A. Tucker (2002).

3.2 Gradle-to-Gate Life Cycle Assessment

Gradle-to-Gate approach to LCA defines the boundary limits for LCA that is from the ore to the product but not further. To perform the LCA the goal and scope of the analysis needs to be defined according to ISO14004:2006 and ISO14040:2006.

The purpose of this LCA study is to examine two Copper processing methods, more specifically the Flash Smelting Furnace with Flash Converter Furnace (FSF-FCF) and Flash Smelting Furnace with Peirce-Smith Converter (FSF-PS) process systems (these will be presented later). The service delivered by the system is one ton of copper while the reference system is a copper process that produces copper from ore where the concentrate consumption in flash smelting furnace is 216.4 t/h (dry concentrate). The values in the results are normalized for 1 kg of Cu which is common practice in LCA.

The system boundaries in this assessment are those defined in the Figure 5. The production system is divided to subsystems of mineral processing, pyrometallurgical processing and hydrometallurgical processing. These subsystems are on the other hand constructed of separate units that can be further analyzed. This is done most importantly for the Flash Smelter part of the model, which is the source of most of the impacts.

[7] See R.L. Cornelissen (1998) p. 1

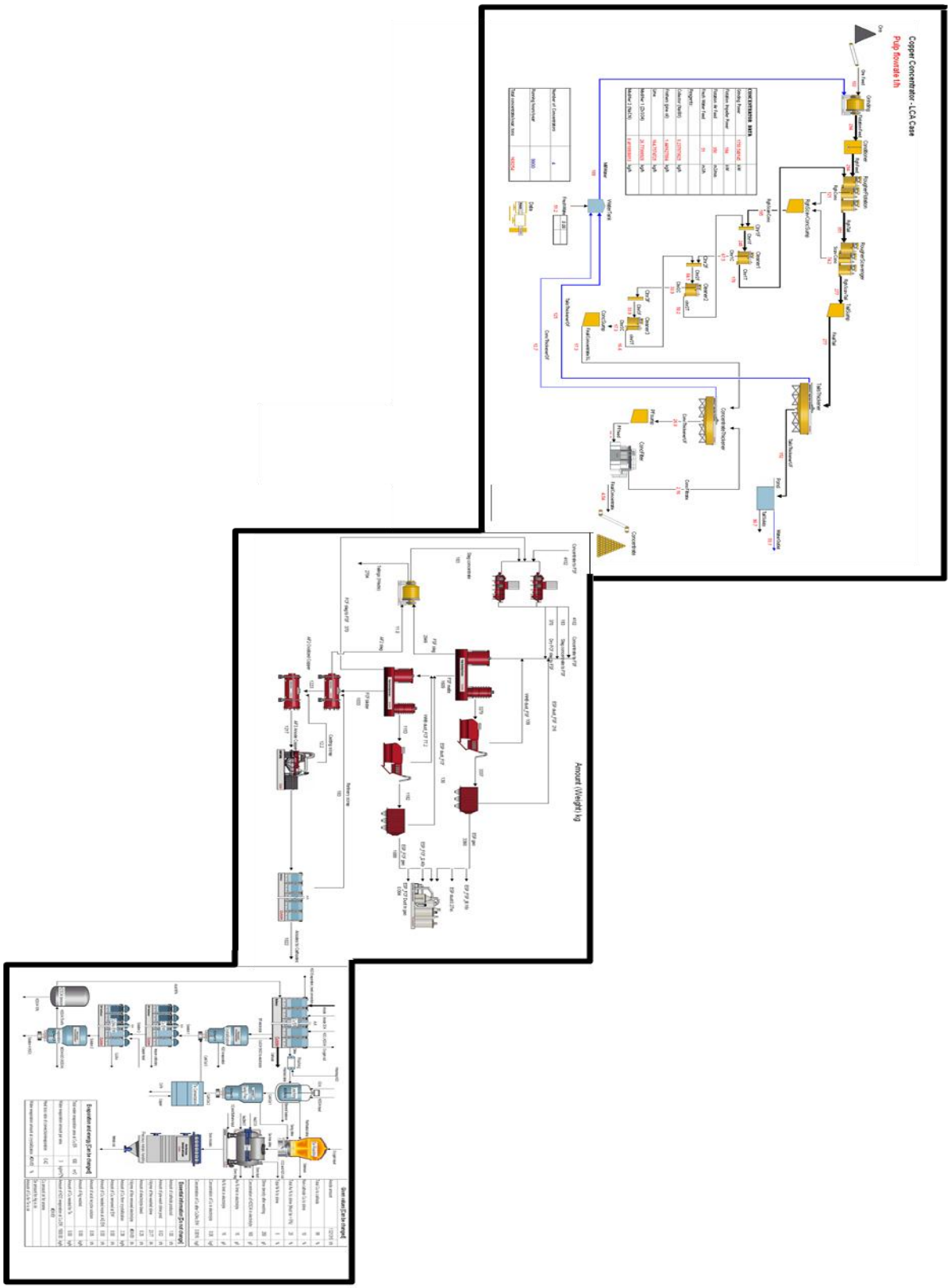


Figure 5, Process model for Flash Smelting Furnace with Flash Converter (FSF-FCF) with system boundaries (HSC-Sim ™)

3.2.1 Assumptions and Limitations

The limitation of assessment is that it only focuses on the production side while the rest of the life cycle is ignored (Copper use and recycling, part of the acid plant). One inconsistency within the model is that the moisture of the concentrate is different in mineral processing subsystem output (5 m-% moisture) compared to pyrometallurgical subsystems input (10 m-% moisture). This inconsistency is solved by assuming that the concentrate collects 5 m-% of moisture during the transportation. This should be noted when analyzing the results.

The acid plant is not taken within the system boundaries in the LCA except the electricity consumption, which explains some of the results. Also the fugitive emissions of FSF-PS process are not taken into account as these were not included to the models.

The variables of interest in Copper Production processes are the power need (separately for electricity and fuels), CO_2, SO_X, NO_X, water consumption, residue, fugitive emissions, Particulate Emissions and Exergy consumption. The environmental indicators of interest are Global Warming Potential (GWP), Acidification Potential (AP), Eutrification Potential (EP), Human Toxicity Potential (HTP), Ozone Layer Depletion Potential (ODP), Photochemical Ozone Creation Potential, (POCP), Aquatic Ecotoxicity Potential (AETP), Abiotioc Depletion (ADP).

The Life Cycle Inventory (LCI) was collected from the HSC-Sim ™ ® process models automatically by using LCA tool that, besides other things, lists the input and output streams information. The data obtained this way needs to be transferred to GaBi by mapping an equivalent stream in the GaBi database. Similarly the streams were allocated according to their origins ie. from/to nature, from/to technosphere etc.[8].

It should be noted in this context that there is a risk that as the consumption and recycling patterns are not included to the assessment there might be a risk of " …environmental sub-optimization, meaning the risk of reducing one impact at the cost of increasing another" (A. Björklund, 2011). While on the other hand from the production perspective the LCA can be regarded as almost comprehensive as the use of GaBi allows experimentation with the sources of resources utilized in production.

[8] See Chapter "Simulation and Analysis" for more details

3.3 Exergy

An exergy is a thermodynamic state property which describes the available work of the system or more precisely the exergy of a system can be defined as the theoretical maximum amount of work which can be extracted from physical system when it is brought to thermodynamic equilibrium with the environment by means of reversible processes (T. Laukkanen et al., 2011, J. Szargut, 2005, 1988, R.U. Ayres et al., 1996). Exergy effectively combines the first and the second laws of thermodynamics, that is the conservation of energy and the increase of disorder (entropy) of irreversible processes and it can be understood as "…distance of the target system from the equilibrium…" (A. Masini and R.U. Ayres, 1996).

The exergy of a system can be constructed from four parts: the physical exergy is the work obtainable from physical properties of a system at p, T, c when it is returned to the reference state at (T_0, p_0, c_0); chemical exergy is the work obtainable from chemical composition of the system at (T, p, c) when it is returned to the reference state composition (T_0, p_0, c_0); kinetic exergy is the work obtainable from the velocity of the system relative to the surface of earth; potential exergy is the height of the system compared to the average level of earth. (A. Massini and R.U Ayres, 1996, J. Szargut, 1988)

Formally this can be written as:

$$B = B_{PH} + B_{CH} + B_P + B_K \qquad \text{Eq. 1}$$

Where B = total exergy, B_{PH} = physical exergy, B_{CH} = chemical exergy, B_P = potential exergy B_K = kinetic exergy.

In practice the kinetic exergy can be ignored when the experimentation is based on static model. In dynamic models the kinetic exergies should be taken into account. Potential exergy on the other hand should be taken into account whenever we have exact information regarding the location of equipments and in broader context the factory but in this case as a simplification the potential exergy is assumed to be zero and only the thermal exergy which is a sum of chemical and physical exergies is taken into account.

3.3.1 Exergy Calculations

In order to calculate the exergy of a system we need to calculate the exergy difference between the system under consideration and the standard environmental state. This requires

calculating the physical work from the change of temperature and pressure as well as work obtainable from chemical reaction heats and changes in concentration. In order to make calculations the reference state that has, in theory, zero-exergy content must be defined. The reference exergies for environmental standard state of elements are in Tables of appendix K that were obtained from J. Szargut (2005). The calculations of exergies represented here are based on J Szargut (2005) and T. Laukkanen et. al (2011).

The calculation scheme for exergy is shown in the Figure 6.

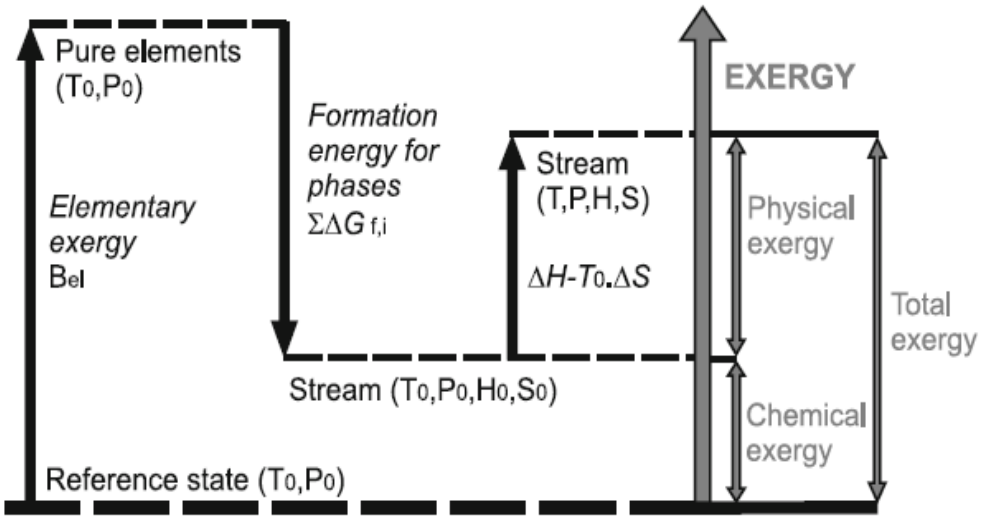


Figure 6, Calculation scheme for exergy

The physical exergy of a substance can be calculated in general form from the equation 2 as:

$$B_{PH} = \Delta H - T_0 \Delta S \qquad \text{Eq. 2}$$

where $\Delta H =$ difference in enthalpy between the system under consideration and the state of environment, $T_0 =$ temperature of reference environment, $\Delta S =$ difference between the system entropy and reference environment entropy. This is used for calculating the exergy available from heating and expansion of the substance under consideration from environmental state to the state under consideration as well as for calculating the similar changes for the reference species from environmental state to the system state under consideration.

If the exergy of mixing was added to this function the exergy equation would require adding the exergies of components together as well as the entropy of mixing should be added to the equation in which case the function would become:

$$B_{PH} = \sum_i \left[H_i - H_{0,i} - T_0(S_i - S_{0,i})\right] - RT_0 \sum_i x_i ln x_i \qquad \text{Eq. 3}$$

or for non-ideal mixtures when activities are used $a_i = \gamma_i x_i$, where γ_i = activity coefficient of ith component:

$$B_{PH} = \sum_i \left[H_i - H_{0,i} - T_0(S_i - S_{0,i})\right] - RT_0 \sum_i n x_i ln a_i \qquad \text{Eq. 4}$$

This will be discussed more in-detail later in this Chapter.

Chemical exergy can be calculated in general form from the equation 5 as:

$$B_{CH} = \sum_{i=1}^{n} x_i(\mu_i - \mu_{i,0}) \qquad \text{Eq. 5}$$

Where x_i = mole (mass) fraction of the ith component, μ_i= chemical potential of species i of the substance in system under consideration and $\mu_{i,0}$ = chemical potential of the species i in the environment.

The chemical potential difference between system and the reference state can be calculated from the equation 6 when activities are taken into account or from equation 7 depending on the reference species and the phase of it when partial pressures are considered (T. Laukkonen, 2011 see equations 15-18):

$$B_{CH} = \sum_i^n x_i(\mu_i - \mu_{i,0}) = RT_0 \sum_i^n x_i ln \frac{\alpha_i}{\alpha_{i,0}} \qquad \text{Eq. 6}$$

$$B_{CH} = RT_0 \sum_i ln \frac{p_i}{p_{i,0}} \qquad \text{Eq. 7}$$

Where R = gas constant (8.314 J/Kmol), T_0 = 298.15 K, α_i = activity of the substance at (T,p,c), $\alpha_{i,0}$ = activity of the substance in environmental reference state, p_i = partial pressure of the substance at (T,p), $p_{i,0}$ = partial pressure of the substance in environmental reference state.

As the values for standard chemical exergies have been tabulated in J. Szargut (2005) and the environment is assumed to be the normal standard environment (T=298.15 K, p=1) the chemical exergy calculation becomes:

$$B^0_{CH,i} = \Delta_f G^0_i + \sum_{el,i} n_{el,i} B^0_{CH,el,i} \quad \text{Eq. 8}$$

Where $B^0_{CH,i}$ = standard chemical exergy of ith element or a compound, $\Delta_f G^0$ = standard normal free energy of formation of ith element or a compound, n_{el} = number of moles of element in the ith compound under consideration, $B^0_{CH,el}$ = chemical exergy of element.

Besides this the mixing of substances is a source of exergy generation which is a part of the chemical exergy. Mixing lowers the exergy as energy is required to separate the substances from each other after being mixed and on the other hand the mixing releases energy as heat. The chemical exergy for mixture can be calculated by using equation 9. (R.L. Cornelissen, 1998):

$$B_{CH,mix} = \sum_i n_i x_i B^0_{CH,i} + RT_0 \sum_i n_i x_i ln\gamma_i x_i \quad \text{Eq. 9}$$

Where we have $B_{CH,mix}$ = Chemical exergy of mixing; x_i = mole fraction of ith component; $B^0_{CH,i}$ = standard chemical exergy of ith component; T_0 = temperature of reference environment; γ_i = activity coefficient (molar) of i:th component.

$$a_i = \gamma_i x_i \quad \text{Eq. 10}$$

a_i =activity

If we replace $B^0_{CH,i}$ from equation 8 and a_i from equation 10 to equation 9 we can write the total chemical exergy as:

$$B_{CH} = \sum_i n_i x_i \left(\Delta_f G^0_i + \sum_{el,i} n_{el,i} B^0_{CH,el,i}\right) + RT_0 \sum_i n_i x_i ln a_i \quad \text{Eq. 11}$$

For single substance streams the equation 8 can be used. For gas and solid mixtures we can make an ideal gas assumption stating $\gamma_i = 1$ and use partial pressures or molar fractions instead and in such case it is possible to use identity $a_i = \gamma_i x_i = x_i$ in which case we can rewrite the equation 9 as:

$$B_{CH} = \sum_i n_i x_i \left(\Delta_f G^0_i + \sum_{el,i} n_{el,i} B^0_{CH,el,i}\right) + RT_0 \sum_i n_i x_i ln x_i \quad \text{Eq. 12}$$

As for aqueous and other liquid systems the activities can vary significantly from values $a_i = 1$ (that is the ideal system) and the use of equation 11 is well justified in such cases. [9]

[9] A calculation example for each case is represented in Appendix L.

The values for free energy are obtained from the HSC ®, the number of moles is obtained from the HSC-Sim ™ models and the chemical exergy of elements from J. Szargut (2005) and updated Tables of R. Rivero and M. Garfias (2006)[10]. The exergy calculation scheme of HSC was based on equation 8 (pyro and hydro models) for the results represented in this Thesis.

3.3.2 Exergetic Efficiency

When analyzing a process system the exergy as such does not provide information on how efficient the process is but instead it provides information on energy and resource uses. To understand the thermodynamic efficiency of process steps as well as the whole process system we need to perform an exergetic efficiency analysis where we compare existing exergy use of a process to the theoretical maximum exergy use. This provides information on how far from the theoretical maximum exergy use we are and it also enables objective comparison between different processes by means of thermodynamic efficiency. (R.L. Cornelissen, 1998)

There have been developed various measures for exergetic efficiency. One method defined by V.M. Brodyansky, M.V. Sorin and P. Le Goff (1994) can be expressed as:

$$\beta = \frac{B_{Tot,out} - B_{tr}}{B_{Tot,in} - B_{tr}} \qquad \text{Eq. 13}$$

Where $B_{Tot,out}$ = outgoing exergy, $B_{Tot,in}$ = ingoing exergy, B_{tr} = transiting exergy which does not change.

Another method which can be regarded as more practical is so called rational exergetic efficiency developed by Kotas (1995) which defines efficiency as ratio between desired exergy output and actual exergy used:

$$\beta_{rational} = \frac{B_{desired}}{B_{used}} \qquad \text{Eq. 14}$$

Where $B_{desired}$ = the sum of all exergy transfers from the system[11], B_{used} = exergy required for performing the desired transformation[12].

The Kotas (1995) exergetic efficiency method can be applied to all the other systems besides dissipative systems. (R.L. Cornelissen, 1998)[13] As the production of copper produces other

[10] See Appendix K
[11] Includes the creation of other substances, heat losses etc
[12] ie. the transformation of copper ores to pure copper.

economically valuable substance the environmental burden needs to be allocated. The environmental burden is allocated to co-products by the distribution of exergy destruction on the basis of changes in the exergy values of the flows. The allocation method starts "…from zero inputs, if possible, and each addition to the exergy destruction is allocated to the marginal increase in the exergy value of the flows" (R.L. Cornelissen, 1998). This assumption allows us to use the concentrations of substances that are co-produced with copper, for allocation of the environmental load for those unit operations that are common while for separate process steps needed to extract wanted valuable materials the load is allocated for that material. (R.L. Cornelissen, 1998)

3.3.3 Exergy Analysis

"The exergy analysis pinpoints the places where the exergy destruction takes place and in the improvement analysis different possibilities can be presented to minimize the life cycle irreversibility". (R.L. Cornelissen, 1998)

Exergy analysis is based on the inputs and outputs of the process (and process units) as well as transformations and compositions of substances. Its purpose is to identify the sources of resource consumption within the system in thermodynamic means, thus it can be used to provide specific and quantified information of the systems efficiency (T. Laukkanen et al., 2011, A. Masini and R.U. Ayres, 1996). For this reason the LCA of a process is convenient to perform together with exergy analysis as it provides information regarding the inputs and outputs. The flow sheets of process models and exergy analysis are created using HSC-Sim ™ while the LCA is performed in GaBi. To combine these two assessments together, data integration between HSC-Sim ™ and GABI is accomplished, thus the analysis is as well a demonstration of using computer models for integrated LCA and exergy analysis.

When performing exergy calculations the reference state on environment needs to be defined. In optimal reference environmental state the exergy would be zero but as this doesn't occur in reality the reference state must be defined separately (Dincer and Rosen, 2007). Commonly used reference state is T=298.15K and p=1bar (J. Szargut, 1988, 2005), which is chosen for this analysis as well. Another requirement for exergy calculations is to define the standard molecular reference species that is chosen for each element. The reference species and exergies proposed by J. Szargut et al. (2005) and additions made by R.Rivero and M.Garfias

[13] For examples on calculating efficiencies see R.L. Cornelissen (1998) pp. 16-20

(2006) [14] were used as basis in the calculations while other methods were rejected for their the non-accurate reference state determination methods (i.e. Ahrendts, 1980, Bosnjakovic,1963). The reference state of element is usually set for the most stable species the element can be found in nature with few exceptions in J. Szargut et al. (2005) work. The standard reference species are defined for each element in one of these phases: air (gas), sea water (liquid) and earths crust (solid). For example coppers reference state has been defined as ionic Cu^{2+} in sea water. The exergies of different substances are calculated from these standard states. (J. Szargut et al. 2005)

For the exergy analysis the exergy recovery that takes place in the acid plant in the form of recapturing the SO_2 is taken into account as it has such great significance for exergy efficiencies while the acid plant resource use was not taken into account as there didn't exists a model for the acid plant.

3.4 Exergetic Life Cycle Assessment

An Exergetic Life Cycle Assesment (ELCA) is a tool to identify the exergy flows within the production system which can be use to "…determine the thermodynamic perfection of a system…" (R.L. Cornelissen, 1998). Not only that the ELCA can be used for evaluating the environmental impacts of the system as well as the exergy losses can be considered as the potential to do work towards the environment. (R.L. Cornelissen, 1998)

In order to perform ELCA instead of LCA we must make an assumption of Zero-exergy emission processes where the emissions are translated to exergy and the final chemical composition of emissions are assumed to be the same as the environment chemical composition. (R.L. Cornelissen, 1998) The exergy calculations are done by using the reference species and Tables created by J. Szargut (2005) as represented in Chapter 4.3.

In ELCA the exergies of streams needs to be defined as the first step. This requires complete information on mass and energy flows and balances at each process step and the standard environment must be defined. This data can be then used to calculate the exergy destruction at each step. This exergy destruction can then be added together for the whole life cycle to determine the irreversibility of the process system.

[14] See Appendix K for reference chemical exergy Tables

The exergy analysis represented in Chapter 4.3.1 can be used to identify the points where the exergy destruction takes place and an improvement analysis can be used to suggest improvements for the system. Also an economic analysis needs to be done but this goes beyond the scope of this Thesis. For definitions see G. Tsatsoronis (2007) and for exergo-economic analysis see for example Lozano and Valero (1993) or F. Petrakopoulou et al. (2011).

The average exergy consumption of whole Copper production is estimated to be 41.8 - 57.3 GJ/t (Bruch et al., 1995) while some smelter specific data on low grade deposits on exergy consumption has given values 47 GJ/t for whole process of which 32GJ/t were required for mining, concentration and transports and rest 15 GJ/t was designated for smelting and refining processes which was later expected to reduce to 7.3 GJ/t due to process up-grades (Landner and Lindeström, 1999).

4 Copper Life Cycle

In this Chapter the Copper and its life cycle will be discussed in more detailed manner. This is required to better understand the importance of copper production process from resource consumption view point and its importance in the ecological footprint of copper use.

In general copper life cycle consists of four main phases; extraction, refining, use and discard or recycling.

Extraction consists of ore mining, grinding and concentration. Currently the grades that are extracted are about 0.5-2% (R.U. Ayres, 2002, Davenport et al., 2011, A. Lossin, 2012). Low grade mines are usually open pits while high grade mines are typically underground mines. The explosives are extensively used in the mining process and the materials handling is using elevators, convoys or huge trucks. The mined particles are then carried for grinding where water is added and the particles of different sizes are crushed to homogenously small particles of sizes varying 20-100 µm depending on the grade of the ore (A. Lossin, 2012). The mining and grinding is rather energy intensive consuming approximately 20-32 GJ/t Cu (R.U. Ayres, 2002). Production of copper ton requires about 50-200 fold quantity of ore processing depending on the grade and thus the mass handling over all is also energy intensive and significant exergy losses can be expected to generate from this (S. Gößling-Riesemann, 2008, R.U. Ayres et al. 2006a,). After grinding frothers and heteropolar reagents are added to the mass and air bubbles are blown through the mass bringing the sulphide minerals to the surface. The overflow is collected and dried. The resulting copper concentrate contains about 30 m-% of copper (Davenport et al., 2011) .

Refining consists of pyro- or hydrometallurgical processing depending on the copper ore quality. Oxides and chalcocite can be processed hydrometallurgically, while other sulphide minerals can be processed pyrometallurgically. In pyrometallurgical processing the resulting “blister copper” needs to be electrorefined using electrolysis, except for the fire refining process which uses nowadays mainly copper recycles as input while in hydrometallurgical processing electrowinning of the electrolyte solution is required. The shares and trends of these different kinds of processing methods are represented in the Figure 7.

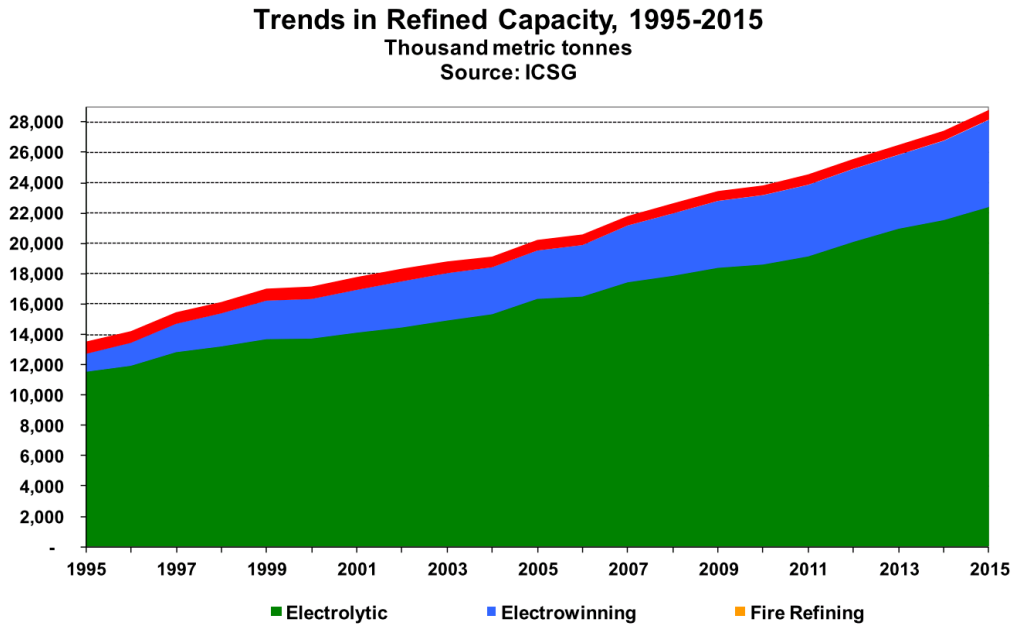


Figure 7, Trends in refined capacity, ICSG (2012)

In pyrometallurgical processing the dry concentrate is possibly pre-heated and then fed to furnace together with sand as a flux and added oxygen that is usually produced locally by cryogenic distillation of air. The oxygen production is one major electricity consumer in the process. The oxygen causes copper and iron sulphides in ore concentrate to oxidize resulting in significant heat generation that enables autogenous production (the details are discussed later in the Chapter 4.2.2 and appendix B) at around 1250-1300C. The oxidization produces sulphur dioxide that is generally collected and processed catalytically to produce sulphuric acid. Dust is collected and reprocessed in furnaces. The oxygen has different affinities on copper and iron in these conditions causing the copper to concentrate into the sulphur rich matte and iron to concentrate into the slag together with SiO_2 flux. The copper rich matte is collected to further processing with oxygen blow where most of the copper sulphides are oxidized to produce blister copper and more of sulphur dioxide for sulphur acid production. This part could be incorporated with the flash smelting or it could be a separate process step. The blister copper is fire refined and cast to anodes that are electrorefined to high purity copper. Valuable metals such as Au and Ag can be collected in electrorefining as by-products. (A. Lossin, 2012, G. Davenport, 2011)

In hydrometallurgical processing sulphuric acid is added to grinded or unground ore from mining. Copper and other oxides solves to the sulphuric acid which is collected. The copper is

then concentrated using copper specific extractants such as oximes. The extracted copper is further stripped by H_2SO_4 to solutions of 45-50 g Cu/l and the solution is finally electrowon. In electrowinning a cathode is plated by using an electric current. (G. Davenport, 2011)

The annual refined copper production by pyrometallurgical processing is approximately 18.5 Mt/a while the production by hydrometallurgical processing is approximately 5 Mt/a while the rest 1 Mt/a is produced by fire refining (ICSG, 2012). The total refined copper production is thus about 24.5 Mt/a (in 2010). According to ICSG (2012) the world copper scrap use was 8.3 Mt/a while the copper recycling input rate was 33.9% .

4.1 Extraction of Copper

The production of copper is capital intensive and besides that requires significant amounts of energy. The Worlds annual copper production has been estimated at 16.2-18 Mt of which more than 12.9 Mt are from smelters and total refined Copper production at 19-22 Mt of which about 20% comes from recycled end-of-use products (G. Davenport et al., 2011, R.U.Ayres, 2002). The grades of mined ore range between 0.5-2 % with average grade of 0.8% (R.U. Ayres, 2002). Estimated landfill generated in ore mining would be in that case around 2025-2250 Mt/a. To avoid transporting this large land mass the concentration and leaching of copper is done usually at the mine and the land masses are collected at the vicinity of the mine. (G.Davenport et al. 2011).

The most important Copper sulphide minerals (that make up 90% of worlds annual Copper production) are chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu5FeS4) and enargite (Cu_3AsS_4) while important Copper oxide minerals (making up 10% of worlds Copper production) are malachite ($CuCO_3$ * $Cu(OH)_2$), azurite ($2CuCO_3$ * $Cu(OH)_2$), cuprite (Cu_2O) and chrysacolla ($CuSiO_3$ * $2H_2O$) (G. Davenport, 2011, R.U. Ayres et al., 2006a)[15]. The processing principles of Copper oxide ores and Copper sulphide ores vary significantly except for chalcocite that can be treated either way (A. Lossin, 2012, G. Davenport, 2011).

4.2 Pyrometallurgical Refining of Copper

The refining of copper sulphides and recycled copper scrap requires typically pyrometallurgical processing. As copper is most commonly found in chalcopyrite, chalcocite and bornite the pyrometallurgical processing consists of about 80% of worlds copper production. The

[15] More comprehensive list of Copper minerals is in Appendix A

pyrometallurgical processing consists of the following steps: mining and grinding, concentration (froth flotation, drying), copper smelting (Flash furnace) and converting (except Direct-to-blister). (A. Lossin, 2012, G. Davenport, 2011, ICSG, 2010)

4.2.1 Grinding

The copper ores are usually subtracted from the ground using explosives (A. Lossin, 2012). The land masses are then transported for autogenous mills or ball mills where the mass is wet grinded to sizes $< 100\mu m$ (A. Lossin, 2012, G. Davenport, 2011)[16]. The power need for grinding follows the Bond's index which suggests that as the Copper deposit grades are falling, and as the grinded particle sizes are decreasing, the power need will grow following equation 15:

$$E = 10 \times W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) \qquad \text{eq. 15}$$

where E= power, W_i = work index, material specific, P=product size in µm, F=feed size in µm.

In the models the power requirement for ore is estimated to be 17 kWh/t, which is professionals estimate for slightly-harder-than-normal rock.

Given this relation the motivation for increasing extracting efficiency from current ores as much as possible should be self evident given that reprocessing of wasted smelter slags and other waste streams as well as processing of low grade deposits could have very significant costs.

The grinded particles are then sent for froth flotation where frothers, most commonly branch chained alcohols (such as pine oil, terpinol or methyl isobutyl carbinol), and heteropolar reagents (such as xanthates) are added to the mass together with water. Xanthates have polar sulphur bond that makes them selective for sulphide groups. Air bubbles are blown through the mass bringing the sulphide minerals to the surface in froths. If pyrite is present the acidity needs to be adjusted with CaO since $CuFeS_2$ floats in basic solutions (pH 7.5-10.5) while for example FeS_2 and PbS do not as hydroxyl ions are more selective on pyrite surface than xanthates. The overflow is collected and dried producing a copper concentrate containing about 30 m-% of copper[17]. (A. Lossin, 2012, G. Davenport, 2011, R.U. Ayres et al., 2002)

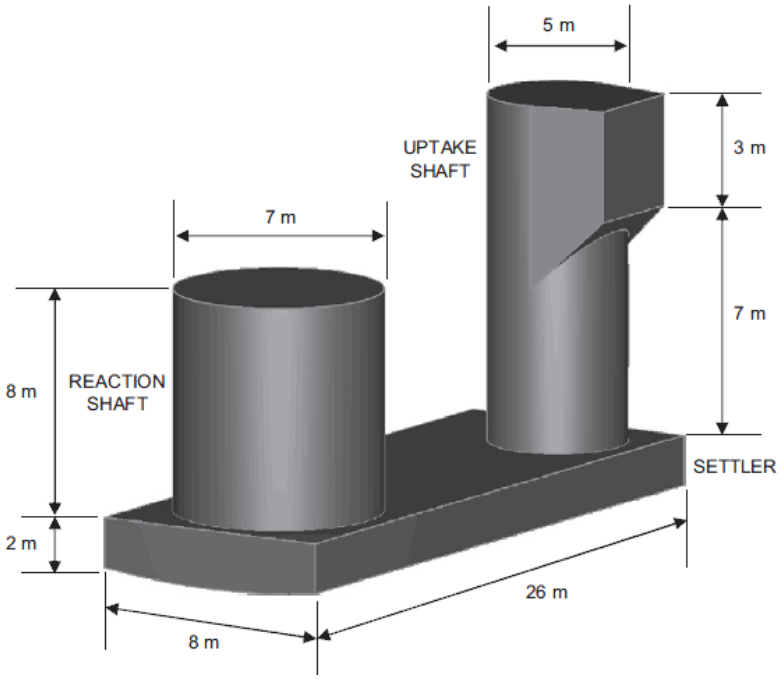
[16] Process diagram for grinding is in Appendix B
[17] Froth flotation flow sheet is in Appendix C

4.2.2 Copper Smelting

There are various ways to process blister copper from 30% copper concentrates. Most used pyrometallurgical smelting technologies are Outotec flash smelting that accounts for more than 50% of Worlds copper production, Ausmelt/Isasmelt, Noranda and Teniente smelting. Besides these it is worth introducing converter technologies such as Peirce-Smith Converting, Outotec Flash Converting as well as Outotec Direct-to-Blister Copper processes. (G. Davenport, 2011)

The basic idea in production of blister copper from concentrate can be described with few chemical reactions. Most importantly sulphides in concentrate need to be reacted with added oxygen. This requires typically two or three steps: roasting, where part of sulphides are oxidized (not necessary); flash[18] or other type of furnace where sulphides are reacted with oxygen to form 60-70 Cu m-% in matte (the chemistry and different processes will be discussed in appendix); converting the rest of the sulphides in matte to sulphur dioxide, iron slag and blister Copper (99% purity) by using oxygen blow in converter. (A. Lossin, 2012, G. Davenport, 2011)

A picture of typical flash smelting furnace is depicted in Figure 6



[18] Flash furnace construction is introduced in Appendix D

Figure 8, Outotec Flash furnace, G. Davenport, 2011, fig. 6.1, p. 90

All the reaction enthalpies are expressed in 25°C if not mentioned otherwise

Following exogenous reactions (for chalcopyrite, pyrite and chalcocite accordingly) occur in molten concentrate in flash smelting furnace increasing the temperatures to above 1200 °C:

$$CuFeS_2 + \frac{5}{2}O_2 \rightarrow Cu + FeO + 2SO_2 \qquad \Delta H = -720kJ\ (1200\,^{\circ}C) \qquad 1$$

$$FeS_2 + \frac{5}{2}O_2 \rightarrow FeO + 2\,SO_2 \qquad \Delta H = -686kJ\ (1200\,^{\circ}C) \qquad 2$$

$$Cu_2S + 0_2 \rightarrow 2Cu + SO_2 \qquad \Delta H = -216kJ\ (1200\,^{\circ}C) \qquad 3$$

These reactions are enough to provide sufficient heat to enable autogenous operation.

To generate two phases some silica is added to the process: iron and other oxides together with silica forms a slag while iron and other sulphides form a matte. SiO_2 addition increases on the other hand heating need of the melt thus increasing energy consumption. The separation is based on higher activity of iron for oxidation reaction compared to copper in the melt which enables the separation of most of the iron to the slag and copper to the matte. This reaction in unbalanced form can be described as:

$$CuFeS_2 + O_2 + SiO_2 \rightarrow (Cu, Fe, S) + FeO \cdot SiO_2 + SO_2 \qquad 4$$

The temperature of all furnaces can be adjusted by altering the nitrogen (inert) gas feed to the furnace. Inert gas will remove part of the heat through off gas that is partly recovered in heat exchangers. (A. Lossin, 2012, G. Davenport, 2011).

4.2.3 Converting

The copper from smelter is not yet pure enough for anode casting because single-step smelting and continuous converting contains up to 1% S and 0.2-0.4% O (G. Davenport, 2010). Though the remaining amounts of these elements are very small yet the amounts are high enough to create significant amount of gas bubbles to the copper which makes it too fragile for casting so most of these needs to be removed (A. Lossin, 2012)

Converting in practice means "…oxidation of molten Cu-Fe-S matte to form molten 'blister' copper (99% Cu). It entails oxidizing Fe and S from the matte with oxygen-enriched air or air 'blast'" (G. Davenport, 2002).

The removal of these substances in conventional Peirce-Smith converter is a two step process where the iron is first oxidized at 1200C by blowing air and oxygen through the Cu-Fe-S matte from smelter. A flux (of silica in case of PS-process or lime in case of flash converting) is then added to the melt to combine with remaining iron to form a slag that can be separated yielding an iron rich slag and relatively pure blister copper. The resulting sulphur dioxide in the offgas is 8-10% while the fugitive emissions are remarkable. (A. Lossin, 2012, G. Davenport, 2010, R.U. Ayres et al. 2002)

The irons reactions occurring in the converter with oxygen can be described as:

$$FeS + 1,5O_2 \rightarrow FeO + SO_2 \qquad \Delta H = -509kJ\ (1200\,^{\circ}C) \qquad 5$$

$$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2 \qquad \Delta H = -1808kJ\ (1200\,^{\circ}C) \qquad 6$$

In the "second step" the oxygen blow is continued so that the remaining Cu_2S (known also as "white metal") is oxidized to form "blister copper" (blisters of SO_2) containing < 0.1 wt % S and about 0.5 wt % of O, and some impurities. The oxidization reaction follows gross reaction (A. Lossin, 2012):

$$Cu_2S + O_2 \rightarrow 2Cu\,(l) + SO_2 \qquad \Delta H = -216kJ\ (1200\,^{\circ}C) \qquad 7$$

While the sulphur in the main reaction when removing sulphur from matte is in practice

$$[S] + O_2 \rightarrow SO_2 \qquad \Delta H = -315kJ\ (1200\,^{\circ}C) \qquad 8$$

To avoid the formation of copper oxide some hydrocarbons are added to the feed so that the oxygen that has dissolved to the "white metal" can be removed (G. Davenport, 2010). The reactions related to this are:

$$H_2C\,(s,l,g) + 2[O] \rightarrow H_2O(g) + CO(g) \qquad 9$$

$$CO(g) + [O] \rightarrow CO_2(g) \qquad 10$$

$$H_2 + [O] \rightarrow H_2O \qquad 11$$

In case of Outotec flash converter there is only one step where lime (CaO) is used instead of silica as a flux and the input feed is grinded matte from flash smelting. The slag is also recycled to flash smelter. A great benefit compared to Peirce-Smith converter is the higher sulphur dioxide content of $> 30\%$ in the off gas and the non-existing fugitive emissions.

After this the resulting copper is cast to anodes. It is worth to notify that the heating while transferring the molten metal for casting requires extensive amounts of energy that is obtained by burning of fossil fuels.

4.2.4 Electrorefining

In electrorefining the cast anodes are set in sulphuric acid electrolyte bath and a current is run through the electrolyte. This causes anode copper to dissolve to the electrolyte solution as Cu^{2+} in $CuSO_4$ (aq). The Cu^{2+} -ions are carried by the electric current to cathode where pure copper is formed. The electrochemical reactions are.

$$Cu \rightarrow Cu^{2+} + 2e^- \qquad E^O = -0.34V \qquad 12$$

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^O = +0.34V \qquad 13$$

Valuable chemicals such as Pt, Ag and Au are recovered with little extra effort from the slime that is formed at the bottom of the electrorefining pool. The valuable metals can make up a significant share of the profitability of the whole copper process. The copper electrorefining requires energy consumption of 260 – 280 kWh per tonne of plated copper which includes also additional power components, while the current efficiency of electrorefining is about 95%. (A. Lossin, 2012)

4.3 Copper Hydrometallurgical Refining

The copper oxides and some sulphides such as chalcocite can be processed using solvent extraction and electro winning (SX/EW-process) which requires initially leaching of the ore. SX/EW-process is second most significant production process of copper which has grown from 14.4% in 1998 to current 17% of global copper production or about 3.7 Mt/a and the share is likely to increase as the decreasing ore grades and copper recovery from waste slags are favorable for SX/EW-process (ISCG, 2012, G. Davenport, 2011, R.U. Ayres, 2002, Simada et al. 1998). The SX/EW-process is not that dependent of reaction heat but instead is based on hydrometallurgical processing where the solubility of metal oxides and some copper sulphides on sulphuric acid enables the separation from ore heaps with low concentrations of copper.

The copper from acidic solution needs to be separated and this is done by using copper specific solvents that are then stripped to generate copper solution viable for electrowinning. The efficiency of SX/EW-process is not as good as in pyrometallurgical processing as average recovery is 62% vs 88% and the electricity consumption is estimated to be accordingly 33.6 GJ/t vs 20.5GJ/t (G: Davenport, 2011, R.U. Ayres et al., 2002)

4.3.1 Leaching

In leaching the ores mined at the copper mines are collected to stocks that are treated with sulphuric acid. The copper and some other minerals dissolves to the sulphuric acid. The ore can be milled as presented in Chapter 4.2.1 as the grinding improves the leaching efficiency and kinetics due to increased surface. Overall the leaching is rather slow process that could take time from days to years depending on the case. Leaching is significant method for treatment of copper oxide minerals and slags while it can be used for some copper sulphide ores that contains iron. Leaching is also preferred choice when the ore copper grade is low ($< 0.5\%$). The copper rich pregnant solution is collected from the bottom of the stock for further treatment. (A. Lossin, 2012, G. Davenport, 2011)

The reactions of Cuprite (Cu_2O) and other copper oxides take place at $pH < 5$ while the mechanism for copper sulphides and native copper is slightly different as "Copper sulphides require the presence of Fe^{3+} and oxidizing O_2" (G. Davenport, 2011). Chalcocite (Cu_2S) and other sulphides require also stronger acidic conditions (pH 1.5-2) for optimal catalytic bacterial activity. The most important reactions of Cuprite and Chalcosite are presented in the following, while rest of the reaction's are represented in the appendix J:

$$Cu_2O + 2H^+(aq) \rightarrow 2Cu^{2+} + H_2O \quad (14)$$

$$Cu_2O + H_2SO_4 \rightarrow Cu^{2+} + SO_4^{2-} + H_2O \quad (15)$$

$$Cu_2S + 0.5O_2 + H_2SO_4 \xrightarrow[Fe^{3+},\ pH \sim 1.5\text{–}2,\ bacteria]{} Cu^{2+} + SO_4^{2-} + CuS + H_2O \quad (16)$$

The acidic solution is collected for solvent extraction where highly dilute copper (1-10g Cu/l) is separated from the pregnant solution.

4.3.2 Solvent Extraction and Stripping

The solvent extraction is actually a two step process where the copper is first extracted using copper-specific organic extractant. This extractant then needs to be removed by stripping to produce suitable copper rich electrolyte solution (45-55g Cu/l) for electrowinning.

In extraction the copper-ions in pregnant solution forms complexes with organic extractants such as aldoximes and/or ketoximes mixture(s) with diluents (such as kerosene) that lowers the used oximes viscosity in mixers (A. Lossin, 2012, G. Davenport, 2011, R.U. Ayres, 2002). The complex formation reaction is:

$$2RH(org) + Cu^{2+}(aq) + SO_4^{2-}(aq) \leftrightarrow R_2Cu(org) + 2H^+(aq) + SO_4^{2-}(aq) \quad 17$$

Where RH is the organic extractant. The formed copper complexes are separated from the aqueous phase by gravitation and the copper rich organic phase is collected for extractant stripping. In stripping the extractant is removed using the strong acid of spent electrolyte (35g Cu/l) and the organic extractant is returned for reuse (A. Lossin, 2012, G. Davenport, 2011). Typical extractant consumption is 2 kg extractant/t Cu (R.U.Ayres et al. 2002). The Copper rich (50g Cu/l) electrolyte is sent for electrowinning.

4.3.3 Electrowinning

In electrowinning the copper in electrolyte solution is electroplated on cathodes made of steel or copper starters from which the copper is then mechanically separated. Annual Copper production by SW/EW-technology is 17% of world production or 3.7 Mt/a (ICSG, 2012). Usually lead in some form, such as cold rolled PbSnCa alloy, is used as anode for its strength, corrosion resistance and corrosion layer conductivity that adds to long lifetime. The electrowinning reaction on cathode is same as for electrorefining producing pure copper from electrolyte:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s), \; E_0\text{=0.34V} \quad 18$$

While the reaction on anode is different from that of electrorefining as water decomposes to form oxygen and hydrogen gases:

$$H_2O(l) \rightarrow 0.5O_2(g) + H_2(g), \quad E_0\text{=-1.23V} \quad 19$$

The theoretical voltage is thus E_0=-0.89V while in reality the voltage need is closer to 2V due to overvoltage, side reactions and Ohmic potential drop giving a total efficiency of around 30%. The power requirement for producing 1t of Copper is about 7.2 GJ/t Cu. (G. Davenport, 2011)

The electrowon cathodes are either sold to markets for manufacturing or alternatively the copper is mechanically separated from the cathodes and then sold, depending on the cathode material. (A. Lossin, 2012, ICSG, 2012, G. Davenport, 2011, R.U. Ayres et al. 2002)

4.4 Utilities and Waste

One of the main sources of pollution in copper refining process comes from the burning of fossil fuels while maintaining stable production conditions for copper furnaces. Oil consumption per metric ton of Copper produced has been in traditional reverberatory furnaces at around 194 kg oil/t or 300 kW of other form of energy depending on the source while modern Outotec flash furnaces could operate at rates of 15-20 l oil/t reducing significantly the consumption of non-renewable resources. (A. Lossin, 2012)

Production of 1 t of pure copper from copper sulphide ores produces also significant amounts of sulphur dioxide (SO_2). Modern Flash Smelter process SO_2 releases are estimated to be about 25 kg SO_2/ 1 t Cu while reverberatory furnaces are by far the most significant source of SO_2 emissions with 2,5t SO_2 released/ 1 t Cu as compared to hydrometallurgical processing where the SO_2 emissions from the SW/EX produces are much less. (IFC, 1998, R.U. Ayres et al., 2002).

The reason for differences in SO_2 emissions can be found in the principles of different technologies: in flash furnaces the sulphide ores are reacted with good efficiency in a closed chamber enabling high SO_2 contents in the off gas while recovery is very efficient at about 93-99 % (R.U. Ayres, 2002, IFC, 1998). In reverberatory furnaces SO_2 is generated from the use of external fossils fuel as well, while the efficiency of recovery for SO_2 is only about 5% because of the diversified SO_2 off gas contents and leaks from the furnaces (R.U. Ayres et al., 2002). This sulphur dioxide needs to be collected for sulphuric acid plant as otherwise it would eventually form sulphuric acid in atmosphere and cause acidic rains. The sulphur dioxide emissions are also regulated for this reason. Co-production of sulphuric acid in non-ferrous processes is very significant amounting 10.3 MT in 1999 which equal for about 17% of world sulphuric acid production (USGS, 1999).

The acid plant energy consumption is dependent on the concentration of the off-gas as dilute solutions require more effort and mass handling to purify.

Besides SO_2 production of H_2SO_4 also the heat of off-gases are utilized in the waste heat boilers associated with the Flash smelting furnace, Flash Converting Furnace as well as the Peirce-

Smith converters. The heat from the molten streams is used for producing steam which can be further utilized within the process. Most importantly the internal use of steam takes place at the Steam dryer units where the steam is condensed while the moisture of the stream is vaporized lowering the water content of the Cu concentrate, which has originally moisture of 5-10%. The internal steam generation and recycle lowers the external energy need of the process. (G. Davenport, 2011, R.U. Ayres et al. 2002)

Challenges associated with copper production are numerous. One such problem is the overburden which has no economic value and which needs to be dumped at the vicinity of the mine. The main problem is the area needed for the waste but not only that the acid rock drainage (ARD) can be significant problem[19] as the sulphide rocks that have contact with air and water can generate acid waste on which the heavy metals of the ore are soluble. The exposed rock could crack and release even more of the acidic waste and heavy metals that are harmful to environment. Other important mining related waste includes dust and explosives residues. (R.U.Ayres, 2002)

Wastes associated with the concentration include the tailings from the flotation, mainly rock but also flotation chemicals, which are stored in the ponds associated with the mine. Some amounts of copper is lost in these streams.

Smelting wastes are rather complex. Significant amount of the inputs to the Smelting are lost in the slag. The slag holds most of the iron and zinc as well as significant amounts of many other valuable metals. Also the gas streams contains significant amounts of some metals contained within the concentrate such as germanium, bismuth, lead, mercury, cadmium, tin, antimony most of which are harmful and are typically recovered and recycled to the process. (R.U. Ayres et al. 2002)

The leaching of ores could cause some amount of metal sulphides to be released to the nature if proper precautions are not taken as many of the metals are soluble to sulphuric acid (R.U.Ayres et al. 2002).

The copper processes produces also other side products such as Selenium, Tellurium, Lead, Antimony, Arsenic and Bismuth which are harmful to the process or environment and needs to be separated from the streams while valuable side products such as Gold, Silver, Platinum and

[19] This is more of a problem of exhausted mines.

Molybdenum are collected through separate processing. Besides these the most significant side stream is the slag which can be currently used in cement and concrete production, abrasive grit, land reclamation, ceramic tile and as iron ore. All of this can be significant for the profitability of a copper smelter. (G. Davenport, 2011)

4.5 Use and Recycling

Copper is one of the most used non-ferrous metal and thus its production and use is of great importance in economical and societal means. The global copper use for end-products has been estimated at 22Mt/a (H.L. Herrero, 2010).

The copper production and copper use are geographically fragmented in such a way that most of mining and production occurs in third world countries while the main source of consumption is in developed world (D. Giurco et al., 2001). The reasons for developing countries being the largest producers are mainly geological. Over all, the produced copper travels on average long distances on rails and seas of the world before being manufactured.

The copper is generally used in electricity, industry and transport and it can be considered as one of the most important infrastructural elements in modern economies relying on electricity where it is used in electric cables and wires, plumbing, home electronics, car radiators etc. (A. Lossin, 2012, G. Davenport, 2011, R.U. Ayres, 2002). Aluminium has been considered as a substitute for copper, but its costs and electricity carrying capacity have this far restricted substitution only to some specific application such as high-voltage lines or car radiators (A. Lossin, 2012). Copper can be expected to be used widely in the society in the future to come.

The copper occurs in different grades in end products. In some applications the copper is as alloys (eg. brass), in some applications copper is used in low grades (eg. electronics) and in some applications copper is used as such (eg. piping). Not surprisingly the high grade copper is easiest to recycle while the low grades are more expensive and brasses are recycled as such. Typical copper recovery rate depends on the geographical location and the recovery rates vary from Africa's 40% to Latin America's 84% (in 1994, according to Van Beers, Bertram, Fuse, Spatari, & Graedel, 2003 and Vexler et al., 2004). The recycled copper (scrap copper) which has entered the anthroposphere amounts approximately 30% of annual copper use equaling 8.3 Mt/a (ISCG,2012). The recycling reduces the demand for raw ore and as the deposits are degrading it is expected that recycled coppers share will grow in the future.

5 Experimental Part: Simulation and Analysis

In this part the simulation methods used for performing the experiments are used. This includes the representation of the HSC-Sim ™ and GaBi simulation programs as well as the improvements that were made on the HSC-Sim ™. After this the process models for FSF-PS and FSF-FCF processes are represented.-

5.1 Introduction

"*A Model is as good as its assumptions*"

-M. Friedman-

Thus to create accurate enough model the assumptions must be well defined. In chemical engineering this requires good understanding of the system, thermodynamics and the processes within the system.

The Thesis uses simulation program HSC-Sim ™ developed by Outotec and the original process models given by Outotec as a base for examining the extraction and refining processes that are the minerals, pyrometallurgical and the hydrometallurgical processes. For the LCA part the data from HSC-Sim ™ was exported to GaBi, LCA tool developed by PE International. By integrating these databases it was possible to archive very precise LCA data on the whole Copper production process. Besides this the use of simulation program enables the adjustments for the values. The values of the existing models needed to be adjusted so that all the streams were normalized for production of one ton of final copper from which internal uses were excluded. The process models that were used in simulations are based on actual processes, theoretical knowledge and years of experimental work in Outotec OYJ. The models can be regarded as representations of the reality. For this reason some of the details such as the distributions of flows or the calculations behind these distributions are not presented as they can be regarded as confidential information.

5.1.1 HSC-Sim ™

HSC is a traditional thermodynamic calculation program developed by Outotec for the past 30 years that has its basis in wide collection of thermodynamic databases for various substances. The HSC-Sim ™ is a process simulation program extension to the HSC, where the units are

drawn on the flow sheet and the streams are connected according to their real life model and the contents of streams are defined.

The HSC has three separate modes for analyzing flow sheets on minerals, pyrometallurgical and hydrometallurgical processes accordingly. All of these modes are needed to create a complete model for process from ore to pure copper.

In “Particles” (minerals processing) mode the main focus lies in the mechanical and statistical properties of the process flows most importantly the size distribution, species distribution and mass of particles. The overall model is built from unit models where these properties can be adjusted. Thus the main operations in Copper process that can be analyzed in this mode are grinding, flotation and concentration to copper concentrate. (HSC 7®, Manual)

In “Distributions” (pyro) mode main focus is in the minerals and distributions. The raw data is available mainly through real life experimentation of pyrometallurgical processes which is then fed to the program which can be used to calculate the overall material and heat balances. This part is used for analyzing drying, flash smelting, converting, gas treatment (heat recovery and dust purification) and fire refining. (HSC 7®, Manual)

Reactions (hydro) mode is based on the chemical reactions occurring in unit operations in solid, liquid, and gas systems. This mode can be used for the electrorefining, electrowinning, washing, crystallization and other such operations. (HSC 7®, Manual)

The LCA add-in of HSC is a tool that allows the generation of input and output streams to and from the system as lists. The key indicators of these streams can be chosen. The streams can be linked to the GaBi database by mapping for performing the actual LCA (see Chapters 1.1 and 5.1.2), thus allowing fast and accurate LCA evaluation of the process as the proper stream data can be used for LCA evaluation instead of average values for streams. The mapping allows the accounting of the input and output streams and is most useful also for the normalization of the stream data for one kilogram of the product.

5.1.2 GaBi

GaBi is a computer based LCA tool developed by PE International that has similarly wide database of environmental indicators for different kinds of substances that allows the calculation of the environmental impacts and indicators of the whole system.

The HSC-Sim ™ ® streams and the GaBi database equivalent were connected by using a mapping tool in HSC that allowed a search for GaBi database to find similar flow. In this tool it was defined if the origins or the destination of the stream was most importantly "from/to technosphere" or "from/to nature". In GaBi those streams that are set to "technosphere" do not count for impacts as they are consumed elsewhere while those streams which are marked as "From/To Nature" make up the environmental impacts of the process. GaBi allows the connection of separate processes to create a complete process model in which all the external impacts can be taken into account such as the transports and energy consumption.

In some cases a similar flow didn't exists in the GaBi database and those streams were not included to the mapping. In other cases the stream contents were not exactly equivalent to the GaBi database but in such cases the closest possible stream was chosen. This could result to some inconsistency of the LCA values.

5.2 Experimentation Section of This Work

In order to provide accurate and coherent results with exergy calculator in HSC 7.0 some modifications were needed to the calculation scheme for exergy.

First of all the initial calculator had 273.15 K as reference point instead of typical 298.15K, which was corrected so that the calculations would be based on same standard state as most of literature.

Secondly the calculation program in HSC 7.0 had a problem in which the standard state for a substance was first chosen for the substance in question only at $T_0 = 298.15K$ but didn't take into account possible definitions for the pressure. This was corrected so that for every substance the standard state was chosen as $T_0 = 298.15K$ and $p_0 = 1bar$.

Thirdly the phase of the substance was needed to be defined more precisely so that the most stabile form was chosen for the substance at $T_0 = 298.15K$ and $p_0 = 1bar$, so that, as an example, water would be liquid in standard state. The phase of a substance in standard state would have significant effect on the division between physical and chemical exergies in calculations and for this reason the exact phase to be used is important knowledge. This is because physical exergy might be more useful than chemical for recovery of heat while chemical exergy might be more useful information from the material use point-of-view. The choice of phase in HSC is not "water proof" as all necessary boiling or freezing point data might

not be available for every substance and for that reason the data that is available for a specific substance is used otherwise.

And finally the lack of the mixing entropy (adding to the physical exergy) and Gibbs free energy of mixing (adding to the chemical exergy) from the equations was corrected. This was done so that the calculation scheme shown in the Chapter 3.3 is followed thus adding the missing pieces to the calculations. A calculation example of this is provided in excel in the appendix L.

There were also some inconsistencies in the water enthalpy calculations of HSC 7.0 ™ and the water enthalpies of models. An extra multiplier in the calculation scheme was found of which information was given to the coders and the corrections were made.

The HSC model streams were connected to GaBi database through mapping as has been discussed before in Chapters 5.1.1 and 5.1.2. The missing data on the fuel and electricity consumptions were gathered from different sources and this data was normalized and added to the models in the HSC-Sim ™ LCA tool and mapped similarly as other streams. After this the flotation, flash smelter and electrorefining models were linked together within the GaBi to sort out the environmental impacts of the processes, which is discussed in Chapter 6.2.3.

Besides these there was the debugging of HSC-Sim ™ as the new feature of LCA was introduced and some problems mainly at calculation and mapping occurred. The actions taken before the system crushes were analyzed and a report was sent for Outotec Pori Research center where the programmers made necessary changes to the program. [20]

5.3 Processes

The process models of interest are Flash Smelting with Peirce-Smith Converting (called as FSF-PS process further on) and Flash Smelting with Flash Converting (called as FSF-FCF process further on) which were chosen as an example because of FSF-PS processes dominance on the copper production and FSF-FCF processes potential as a technology. Also the availability of data on these processes was one cause for choosing these processes as an example which was necessary to perform this detailed analysis. All of the models used here (flotation, both flash smelters and electrorefining) are based on Outotec's design models which were further supplemented from the external fuels and electricity part.

[20] A short description of fixed problems and suggestions made can be found in the appendix Q

The minerals processing part was based on 950t/h of ore input and 41.9t/h production of concentrate with 5 m-% of moisture. The pyrometallurgical models (FSF-FCF- and FSF-PS-processes) were based on input feed of 240.4 t/h of concentrate with moisture of 10 m-% and copper content of 25 m-% for dry concentrate. The original hydrometallurgical electrorefining model was based on blister copper feed of 58.0 t/h and the (net) production of 56.9 t/h of pure copper.

All of these values were then corrected for 1 kg gross copper production (100%) by using backward induction starting from electrorefining. The values from electrorefining blister copper input after corrections were then adjusted for the desired blister copper output from FSF-PS and FSF-FCF processes. The value of concentrate input on pyrometallurgical part was then transferred to mineral processing output and the values were adjusted accordingly. The multipliers that were used and the logic behind those are discussed in the results. The difference between concentrate moisture in concentrate output from minerals processing was 5% and in pyrometallurgical process input it was 10%. This difference was solved in the calculations by setting the dry concentrate amount equal in both processes and it is assumed that the concentrate is collecting moisture during the transport for making the model easier for analysis. As the point was to define the values for 1 t Cu production the scale factors had to be ignored (and values adjusted accordingly) to keep the distributions similar and some adjustments for the controls had to be considered.

5.3.1 Flotation

The original flotation model that was used was created on the basis of a real flotation process. The initial copper content of the ore in this model was assumed 1.1% and the ore feed was 950t/h while the resulting copper concentrate had a copper content of 25%. These values were normalized for 1 t gross copper production after electrorefining.

The flow sheet of the mineral processing is represented in the Figure 9.

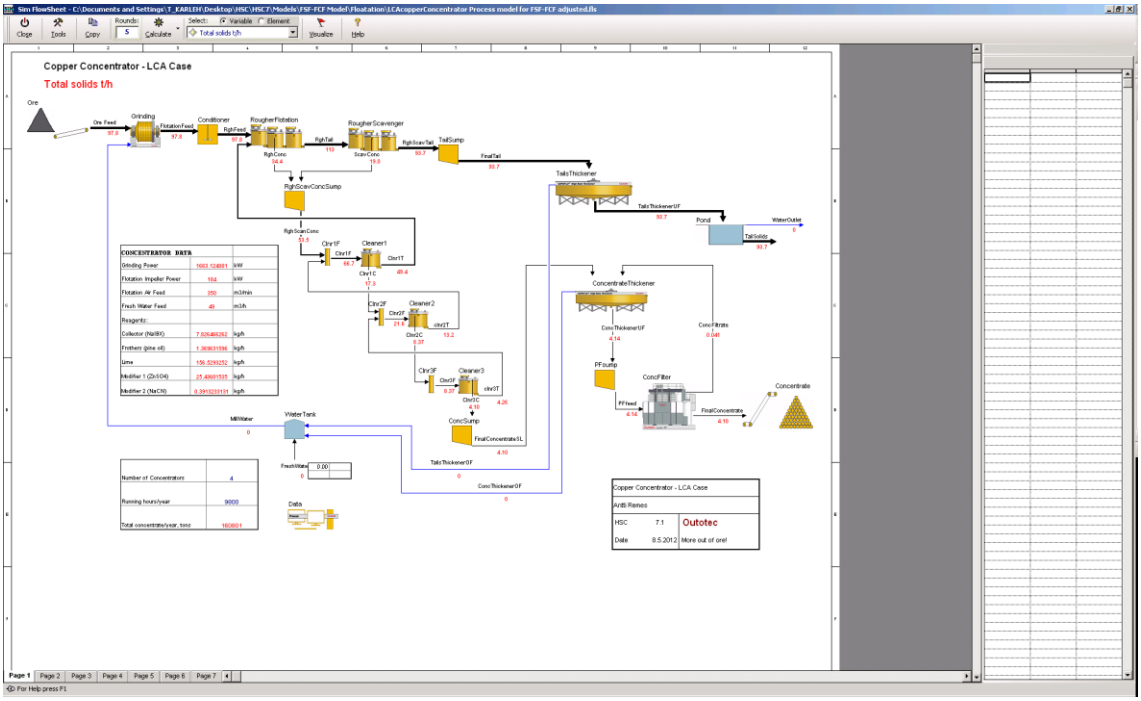


Figure 9, Flotation mass flows for FSF-FCF process model (HSC-Sim ™)

The process units represented in the flow sheet are Cleaners (1-3), Cleaner feeds (Clnr 1-3F), Grinding, Conditioner, Rougher flotation, Rougher Scavenger, Tails Thickener, Concentrate Thickener, Rougher Scavenger Concentrate Sump, Concentrate Sump, Pressure filtration sump (PF sump), Concentrate Filter, Water tank and Pond.[21]

The moisture of dried concentrate from the flotation is 5%. The concentrate from flotation is sent to flash smelter while the ore part is dumped at the mine as well as part of the process water while the rest is recycled. The transportation of concentrates to the smelter could be added at the GaBi to the process flow so that it would be part of the LCA.

5.3.2 Flash Smelting Furnace with Flash Converter Pprocess

The original Flash smelter process model on which these values are based, had 227.8 t/h concentrate in-flow (and 10% moisture). The process values were adjusted for 1 t gross copper production after electrorefining which is discussed in detail in the results.

The flow sheet of the FSF-FCF process is represented in the Figure 10.

[21] A complete list of units can be found in the Appendix M

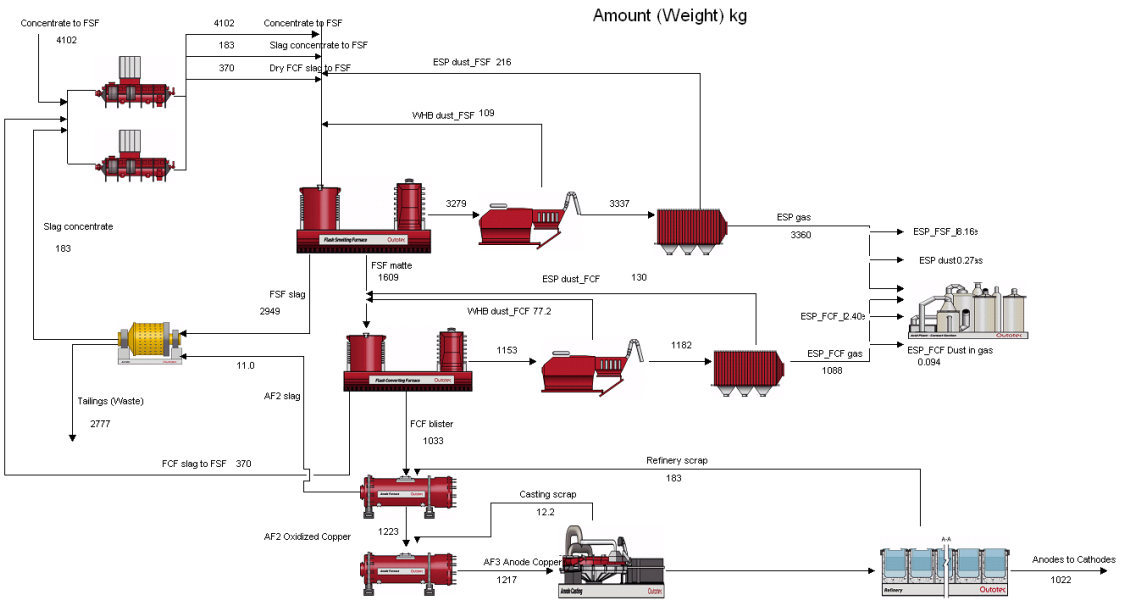


Figure 10, FSF-FCF process flow sheet, mass flows (HSC-Sim ™)

The process units for the FSF-FCF process are presented below[22]:

Steam Dryers (SD), Flash Smelting Furnace (FSF), Flash smelting matte granulation (FSF Matte granulation), Matte Drying unit (Matte drying), Flash Converting Furnace (FCF), Flash converter slag granulation (FCF slag converter), Anode Furnace for Oxidation (AFOX), Anode Furnace for Reduction (AFRE), Anode Casting unit (anode handling) and gas treatment which consists of waste heat boilers (WHB) and electrostatic precipitation (ESP units). Besides these there is virtual mixers in connection to steam dryers (SD mixer), which are not shown in the general flow sheet, and an Acid plant that is regarded as a dummy model which is taken into account only when the recovery of SO_2 is concerned.[23]

5.3.3 Flash Smelting Furnace with Peirce-Smith Converter

To have comparable results a similar sized input of 227.8 t/h of concentrate (with moisture of 10%) for flash smelter was chosen for Peirce-Smith process.

The flow sheet of the FSF-PS process is represented in the Figure 11.

[22] The units in the list follows the format: Unit name (unit code). The unit code might refer to more than one unit, which are not be presented in this flow sheet.
[23] The complete list of units can be found in Appendix M

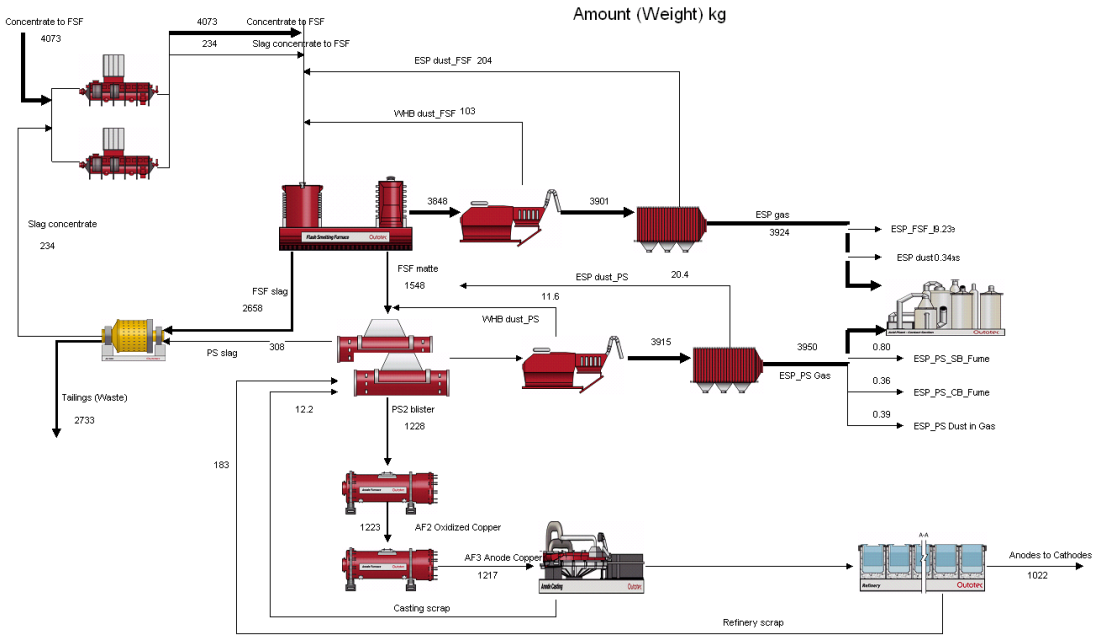


Figure 11, FSF-PS process flow sheet, mass flows (HSC-Sim ™)

The process units of FSF-PS process are listed below[24]:

The process consists of Steam driers (SD1 and SD2), Flash Smelting Furnace (FSF), Peirce-Smith Converters (PS), Anode Furnace for Oxidation (AFOX), Anode furnace for Reduction (AFRE), Casting unit and gas treatment lines which consists of waste heat boilers (WHB) and electrostatic precipitation (ESP units). Besides these there is the Sulphuric acid production plant which is considered as a dummy where only the SO_2 is utilized but no further details are used. The cast anodes of from anode copper are forwarded for electrorefining which is discussed in the following Chapter. The same assumptions apply for the acid plant of FSF-PS process as were applied for the acid plant of FSF-FCF process. [25]

It is worth mentioning that the FSF-PS process has typically leaks of flue gases into the nature that could be some 1- 5% of the flue gas volume (EPA, 1980). In the FSF-PS model that was used no such leaks were included and for this reason the results should be observed with a care.

[24] The units in the list follows the format: Unit name (unit code). The unit code might refer to more than one unit, which are not be presented in this flow sheet.
[25] The complete list of units can be found in Appendix M

5.3.4 Electrorefining

The original electrorefining model was based on 56.9 t/h of pure copper production. These values needed to be adjusted for gross production of 1 kg of copper. The net cathode copper production is 1.0026t/t Cu which is balanced by internal copper use of 0.0026 t (or 2.6 kg) in tellurium cementation so that the gross Cu production is exactly 1 t/t Cu as it should be. The process mass flow is shown in the Figure 12.

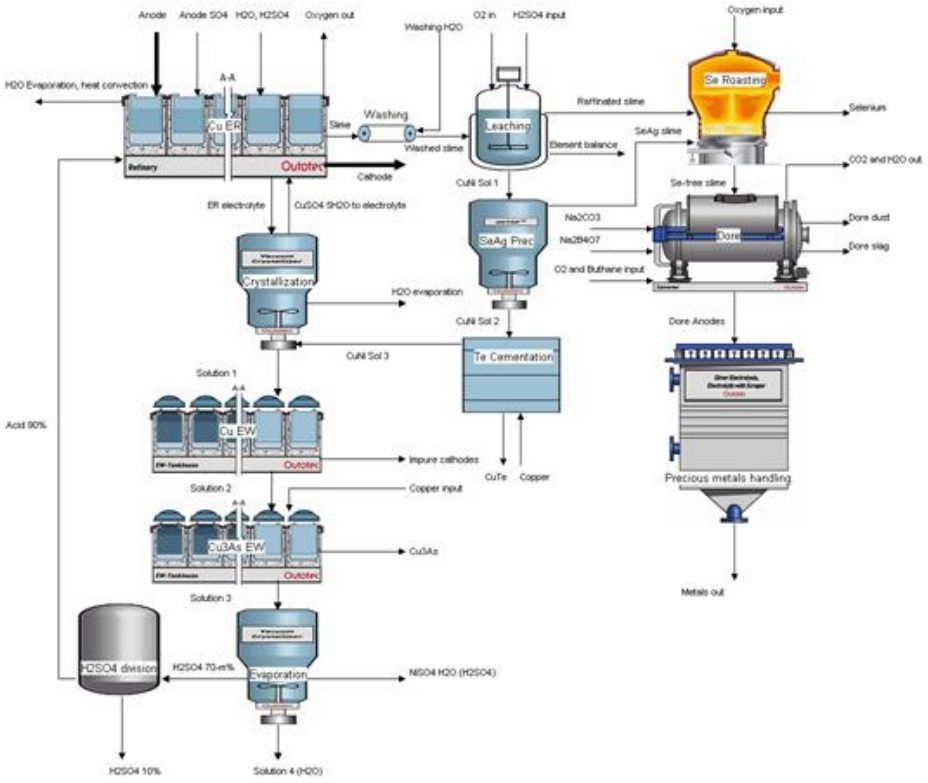


Figure 12, Outotec electrorefining process (HSC-Sim ™)

The process consists of copper electrorefining (CuER) [26], Washing, Leaching, Selenium Roasting (Se Roasting), Dore casting (Dore), precious metals electrorefining (Precious metals handling), Selenium silver precipitation (SeAg Prec), Tellurium cementation (Te cementation), Crystallization, Copper electrowinning, Domeykite electrowinning (Cu_3As), Evaporation and H_2SO_4 concentration (H_2SO_4 division) units.[27]

[26] The purpose of the unit and name in the flow sheet.
[27] A complete list of units and names can be found in the Appendix M

5.4 Assumptions, Definitions and Possible Sources of Model Errors

There were numerous assumptions made within the models which should be mentioned so that the models can be analyzed correctly. It should be mentioned that the models are based on the best available data and thus some of the values are subject to debate, especially the external fuel consumption values. The assumptions and imperfections of the model are represented here for process models, mapping and exergy.

Process models:

1. The process models were based on actual processes, theoretical knowledge and years of experimental work and as such those are assumed to be fair representations of the real processes.
2. External fuels are fuels which are not initially included to the original models and needed to be estimated. They are used for stream heating and other similar purposes.
3. The external fuels and electricity use of the flash smelter and acid plant were based partly on A. Vartiainen (1998) internal report as well as estimated values for the Smelter A copper smelter.
4. The use of explosives, mill rods & balls and transports from the mine are not taken into account for energy and exergy calculations.
5. The power need of 17 kWh/t for ore grinding is based on professional estimate for harder than usual rock, while the power requirement for impellers for flotation are based on installed power of motors.
6. An assumption was made that the concentrate collects 5 m-% of moisture during the transport.
7. Typical fugitive emissions from FSF-PS smelter were ignored
8. Steam and water circuits are not know from the process and for this reason the water inputs and outputs are either feed or products while in reality this might not be the case as the water circulates in the processes.
9. Water circuits needs to be added to the model in order to make the model complete.
10. Minerals processing model was based on original model with 950 t/h of ore with 1.1 m-% Cu concentration and 41.9 t/h of 25 m-% copper concentrate production with 5 m-% moisture. Pyrometallurgical models were passed on original model with 240.4 t/h of 25 m-% copper concentrate and 10 m-% of moisture. The electrorefining model was

based on 58.0 t/h of blister copper feed and 56.9 pure copper net output, all of which were adjusted for gross 1 t copper production.

11. The amounts are adjusted from the original models for production of 1 t of final product copper, thermodynamic data is found from HSC database and exergy calculations are based on the HSC database values and equation 8. The basis for values for chemical exergy of elements is J.Szargut (2005) Tables.
12. The cryogenic oxygen production energy consumption was assumed to be 360 kWh/t O_2 based on literature values (IPCC, 2005, IEA, 2007 and I. Najdenov et al., 2012) and professional opinion.
13. Electrorefining energy consumption was assumed to be 270 kWh/t Cu which was based on A. Lossin (2012) and professional estimates.

Mapping:

14. The mapping was based on the best available combinations of HSC stream and GaBi database.
15. There were streams in HSC that didn't have proper equivalent in GaBi database in which case the stream was either not mapped or the closest possible mapping was created.
16. The fuels were not mapped as they are taken into account when the off-gases are mapped. This was done in order to avoid double accounting.
17. In mapping "technosphere" refers to the anthropogenic use or production while "nature" refers to direct impact to the nature.

Exergy

18. The reference temperature for exergy is 298.15 K and 1 bar.
19. Exergy calculations for flotation were made by hand and are based on the mineral composition of the streams.
20. Some mineral exergies didn't exist in the HSC database and for such chemically similar substances thermodynamic data were used (Sphalerite ((Zn,Fe)S) and Anorthite ($CaAl_2SiO_8$))
21. Zero-exergy assumption leaves the minerals with no economical value out from the analysis. This assumption is generally made for the exergetic efficiency evaluations of

the flotation unit operations. An exception is made for grinding for which no chemical changes occur and the efficiency of power used for grinding is regarded as a proportion of the total exergy of the ore.

22. The energy of electricity was transformed to exergy in ratio 1:1.
23. The recovery of SO_2 is taken into account in the exergy calculations based on the recovery rate of SO_2 in acid plants.
24. Exergies related to area formation or destruction are not included to the exergy calculations.
25. Small differences in the model values when the exergy losses are calculated by unit or at the boundaries are due to small inconsistencies in calculation methods or rounding errors.
26. The exergetic efficiency was based on the actual purpose of process units and thus on the definition of the product stream for each process unit.
27. Various exergetic efficiencies are used for analysis.
28. The exergies related to the electricity consumption are not taken into account in this research.

6 Results and Discussion

In this Chapter the assumptions that were required to get the results are discussed so that the results can be evaluated critically. As the models were not complete the results presented here should be considered as preliminary results, not definitive. The preliminary LCA of copper production and the methods that were used for normalization are discussed. The preliminary energy consumption of the processes is represented. The preliminary Exergy analysis and its results are introduced in detail.

6.1 Life Cycle Assessment (LCA)

The life cycle assessment consists of the resources inventory, which is automated feature of LCA tool of HSC-Sim ™. Some adjustments for the model values were required to get normalized values for 1 t Cu production. Besides this the energy consumption of the processes needed to be addressed as part of the preliminary environmental impact assessment to get the environmental indicators required for the LCA.

6.1.1 Resource Consumption

The LCA tool of HSC-Sim ™ allowed normalization based on the product available from the flow sheets. Now as the flow sheets are separate it was required to use backward induction to solve the correct multipliers for stream values of Flash Smelting and Flotation flow sheets. Also the electrorefining required a multiplier for the stream values as the internal use of copper for cementation the Cu_3As was taken into account, thus increasing the actual copper production by the equal amount so that the gross copper production of 1 t could be reached.

The input value of anode copper for electrorefining was used as a multiplier to correct output value for the Flash Smelting. As the moisture of concentrate from flotation had 5 m-% of water according to the provided model while the input concentrate in Flash smelting model had 10 m-% of moisture the multiplier was decided according to dry concentrate mass flow and an assumption of moisture gain of 5 m-% in transportation was made.

The normalized values required multipliers so that the inputs of one process model were corresponding to the outputs of one process model so that in the end the final product would be 1 kg of copper. The multipliers used are presented in Table 1 for both, FSF-FCF and FSF-PS models:

Table 1, Used normalization multipliers for values

Process	FSF-FCF	FSF-PS
Electrorefining	1.0026	1.0026
Flash Smelting	1.0225	1.0225
Flotation	4.1017	4.0726

By using the multipliers found in the Table 1, the following results represented in Tables 2 and 3 for the inputs and outputs of flotation part of FSF-FCF and FSF-PS processes were gained:

Table 2, Input feeds for FSF-FCF and FSF-PS flotation models (HSC-Sim ™)

Process	FSF-PS	FSF-FCF	
Stream content	Amount	Amount	Unit
Ore	97.1	97.8	kg/kg Cu
Water	48.3	48.6	kg/kg Cu

Table 3, Output feeds for FSF-FCF and FSF-PS flotation model (HSC-Sim ™)

Process	FSF-PS	FSF-FCF	
Stream content	Amount	Amount	Unit
Water	50.10	50.46	kg/kg Cu
Ore	93.07	93.74	kg/kg Cu
Concentrate	4.29	4.32	kg/kg Cu

Normalized inputs and outputs for the FSF-FCF process were then solved which are represented in the Tables 4 and 5.

Table 4, Inputs of FSF-FCF process (HSC-Sim ™)

Stream content	Amount	Unit
Silica flux	0.57	kg/kg Cu
Air (2 m-% water)	3.62	kg/kg Cu
Conc. Technical Oxygen (95%)	1.40	kg/kg Cu
Concentrate moisture	0.52	kg/kg Cu
Lime Stone	0.13	kg/kg Cu
Concentrate (dry, 25 m-% Cu)	4.10	kg/kg Cu
Fuel Oils	0.06	kg/kg Cu
Natural Gas	0.0007	kg/kg Cu
Propane	0.014	kg/kg Cu
Electricity	4.09	MJ/kg Cu

Table 5, Outputs of FSF-FCF process (HSC-Sim ™)

Stream content	Amount	Unit
Flue gas	0.47	kg/kg Cu
Heavy metal dust	0.011	kg/kg Cu
Carbon dioxide	0.16	kg/kg Cu
Blister Copper	1.02	kg/kg Cu
Acid gas (appr. 38 m-% SO_2)	4.45	kg/kg Cu
Water	0.021	kg/kg Cu
Steam dryer off-gas (46 m-% water)	1.48	kg/kg Cu
Tailings	2.78	kg/kg Cu
Heat Loss	6.62	MJ/kg Cu

The mass balance of FSF-FCF had less than 0.01% inconsistency (inputs 10.41 kg/kg Cu, outputs 10.40 kg/kg Cu), which could be explained by possible rounding errors or other inconsistencies within the model. The calculation methods for energy consumption and external fuels use are represented later in the Chapter 6.

Similarly for the FSF-PS process the values for inputs and outputs when standardized for 1 kg of Cu (100%) after electrorefining can be found in Tables 6 and 7.

Table 6, Normalized inputs of FSF-PS process

Stream content	Amount	Unit
Silica flux	0.61	kg/kg Cu
Air	5.30	kg/kg Cu
Conc Technical Oxygen	0.90	kg/kg Cu
Fuel Oil	0.004	kg/kg Cu
Natural gas	0.005	kg/kg Cu
Light fuel oil	0.024	kg/kg Cu
Propane	0.015	kg/kg Cu
Coke	0.014	kg/kg Cu
Moisture in feed (11 m-%)	0.48	kg/kg Cu
Concentrate (dry, 25 m-% Cu)	4.07	kg/kg Cu
Electricity	4.14	MJ/kg

Table 7, Normalized outputs of FSF-PS process

Stream content	Amount	Unit
Flue gas	0.35	kg/kg Cu
Dust	0.011	kg/kg Cu
CO_2	0.025	kg/kg Cu
Blister Copper	1.02	kg/kg Cu
Sulphuric aerosol (25 m-% SO_2)	7.87	kg/kg Cu
Steam-dryer off-gas	1.37	kg/kg Cu
Tailings	2.74	kg/kg Cu
Heat Loss	6.57	kg/kg Cu

The tolerance of iterative mass balance calculations of HSC-Sim ™ was 0.0000000025%, which can be neglected. The energy consumption of the process will be discussed in the results.

The inputs and outputs of electrorefining are presented in the Tables 9 and 10:

Table 8, Inputs of Electrorefining

Stream content	Amount	Unit
Anode Copper	1.02	kg/kg Cu
H_2O, H_2SO_4 (0.66%)	2.45	kg/kg Cu
Anode SO_4	0.0002	kg/kg Cu
Oxygen	0.003	kg/kg Cu
Na_2CO_3	0.0005	kg/kg Cu
$Na_2B_4O_7$	0.001	kg/kg Cu
H_2SO_4	0.031	kg/kg Cu
Water	0.056	kg/kg Cu
Electricity	0.97	MJ/kg Cu

Table 9, Outputs of electrorefining

Stream content	Amount	Unit
Oxygen	0.004	kg/kg Cu
Water	2.48	kg/kg Cu
Cu_3As	0.07	kg/kg Cu
$NiSO_4$, H_2O, H_2SO_4 solution	0.04	kg/kg Cu
Selenium	0.003	kg/kg Cu
Heavy metal dust	0.003	kg/kg Cu
Slag	0.01	kg/kg Cu
CO_2, H_2O	0.002	kg/kg Cu
Sulphuric Acid 98%	0.01	kg/kg Cu
CuTe	0.002	kg/kg Cu
H_2SO_4 70%	0.03	kg/kg Cu

On this basis the LCA, energy and exergy analyses were possible to perform. It should be noted that the names of the streams are those found in the models while for the water, air and fuels the stream values are combined. The fuel values don't take into account the external fuels which are included to the model separately later in the Chapters 6.2.3 and 6.2.4.[28]

6.1.2 Energy Consumption

The energy consumption of FSF-FCF process has been divided in sections according to the flow sheets. The first part is the flotation part, where the electricity is used for grinding and flotation. The use of explosives and transport of ores from the mine to the flotation plant are not taken into account for the energy use here.

The second part is the FSF-FCF process where the energy is used in the form of fuels within the process as process materials, external fuels for keeping some of the streams molten and electricity in various uses such as in the oxygen production which is not shown in the flow sheets but is included to the system or in the acid plant which is a part of the total flow sheet.

The third part is the electrorefining part that consumes energy for the electrorefining of copper into pure copper plates. The form of energy that is consumed is only electricity.

The flotation process electricity consumption consists of two main sources: the grinding and the flotation. An assumption for work index based power use is 17 kWh/t for the ore grinding and this is based on equation 1 represented in Chapter 4.2.1. The assumption on which the value is based is slightly-harder-than-usual rock. It should be noted that the exact assumptions and values behind the work index based power use are not know for the author and the value is considered as a feature of the model. The power-requirement of the impellers that are used in flotation process is based on installed power of motors.

The energy values that are being used for copper production are varied. There are two cases represented for energy consumption of copper production for this reason.

The first case represents a Flash Smelting (using 31% copper concentrate) that is based on the report by A. Vartiainen (1998) which has been made for internal use of Outotec. It is worth mentioning that the concentrate that was used in the HSC-Sim ™ model had 25 m-% of copper

[28] The list of streams can be found in the Appendix P for whole process

concentrate so there is a significant gap between the model and A. Vartiainen (1998) energy values, especially the fuel consumption. For this reason another case is represented.

The second case is based on calculations of Outotec employees for Smelter A copper production plant energy consumption from which the fuel consumption is used together with the electricity consumption from A. Vartiainen report (1998). This would give us a good approximation of Flash smelter as the fuel consumption of A. Vartiainen report (1998) could possibly underestimate the fuel consumption. The consumption of "other fuels" in case of FSF-FCF process (Smelter A) is adjusted to be equal to the share of "other fuels" in model of FSF-FCF (Vartiainen) compared to FSF-PS (Vartiainen) giving a multiplier of 1.77/1.82=0.97.

Some of the values used in energy calculations were obtained by using the models and literature. The fuels that are used directly within the process are taken from the model and these values are included to the energy calculations by transforming the net calorific values obtained from HSC thermodynamic calculator. The values are those found in the Tables 10 and 11.

The cryogenic oxygen productions energy consumption was assumed to be conservative 360 kWh/t O_2 as the values for oxygen production were varying between 310-396 kWh (IPCC, 2005, IEA, 2007 and I. Najdenov et al., 2012) and using the values from the models the oxygen production energy consumption could be defined for separate processes. For electrolysis the electricity consumption was assumed to be 270 kWh/t Cu on the basis of A. Lossin (2012) estimate of 260-280 kWh/t Cu while G. Davenport represents even higher values of 300-400 kWh/t. A. Lossin (2012) values were chosen since those were more in line with Outotec's process engineer'-s estimates for the electrolysis. It should be noted that both energy consumption cases includes the slag concentrator which is not directly represented in the FSF-FCF and FSF-PS flow sheets.

The calculations for FSF-FCF and FSF-PS processes are represented in the Tables 10 and 11, where the values are based on alternative case evaluations based on Vartiainen (dark blue) and Smelter A (light blue)[29] for different fuel consumption conditions. The most significant values are represented in dark red[30].

[29] This colour scheme has same meaning in various tables in this Thesis.
[30] This colour scheme has same meaning in various tables in this Thesis.

Table 10, FSF-FCF process energy consumption with different assumptions

FSF-FCF Process Energy Consumption	Vartiainen	Smelter A
	MJ/kg Cu	MJ/kg Cu
Fuels		
Process	1.47	1.47
Other	1.77	5.23
Total	***3.23***	***6.69***
Electricity		
Flash smelter electricity	1.33	1.33
Oxygen production	1.81	1.81
Acid plant	0.66	0.66
Secondary and fugitive gas handling	0.10	0.10
Secondary cooling	0.19	0.19
Total	***4.09***	***4.09***
Total Flash smelting	**7.32**	**10.78**
Electrolysis	**0.97**	**0.97**
Flotation and grinding	**6.65**	**6.65**
Total Energy consumption	**14.95**	**18.41**

Table 11, FSF-PS process energy consumption with different assumptions

FSF-PS Process energy consumption	Vartiainen	Smelter A
	MJ/kg Cu	MJ/kg Cu
Fuels		
Process	0.22	0.22
Other	1.82	5.38
Total	*2.04*	*5.60*
Electricity		
Flash smelter electricity	1.51	1.51
Oxygen production	1.17	1.17
Acid plant	1.18	1.18
Secondary and fugitive gas handling	0.10	0.10
Secondary cooling	0.19	0.19
Total	*4.14*	*4.14*
Total Flash smelting	**6.17**	**9.74**
Electrolysis	**0.97**	**0.97**
Flotation and grinding	**6.60**	**6.65**
Total Energy consumption	**13.75**	**17.36**

The values calculated in the table 11 are giving upper and lower limits for the process energy use. These values do not include internally used fuels, which were included as inputs in the chapter 6.1.1.

6.1.3 Life Cycle Impact Assessment

After the stream data was mapped at the HSC side by the origins and impact category it was transferred to GaBi in the format of ecospold-file. At the Gabi side the processes were connected together. This made it possible to obtain directly from the program the desired environmental indicators that were required for the LCA. The preliminary results are shown in the Figures represented in this Chapter. As this was rather a demonstration of technology not all results are shown. Two models for the whole FSF-FCF process were created in GaBi (using Smelter A and Vartiainen values). The results, which are shown in the Figure 13, were obtained for Global Warming Potential (GWP) and Acidification Potential (AP), Eutrophication Potential (EP) and Ozone Layer Depletion Potential (ODP) for FSF-FCF (Vartiainen).[31]

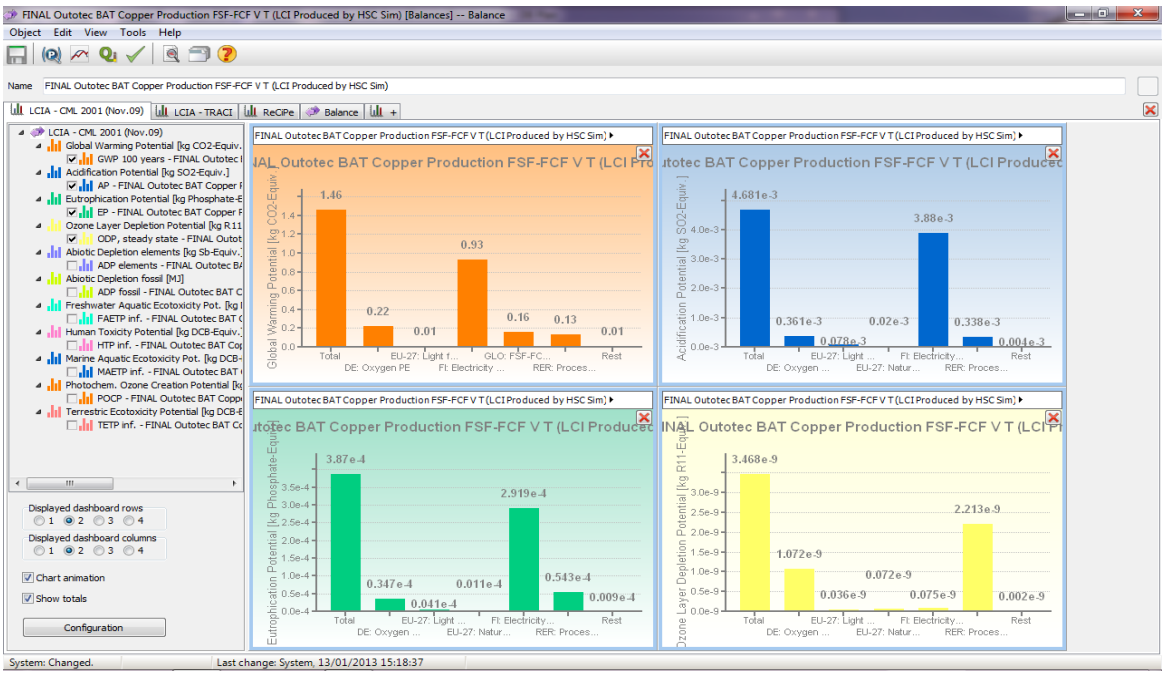


Figure 13, GWP, AP, EP and ODP for FSF-FCF (Vartiainen) process (GaBi)[32]

From the columns the source of the impact can be analyzed and it can be noticed that the electricity consumption seems to be the source of most of the impacts in the process as the

[31] As the Acid plant and fugitive emissions are not fully included no definitive statements can be made.
[32] No Acid plant or fugitive emissions included to these values

FSF-FCF process itself is most significantly contributing to the Ozone Layer Depletion potential indicator. Besides these the energy flow is represented in the Sankey-diagram in Figure 14

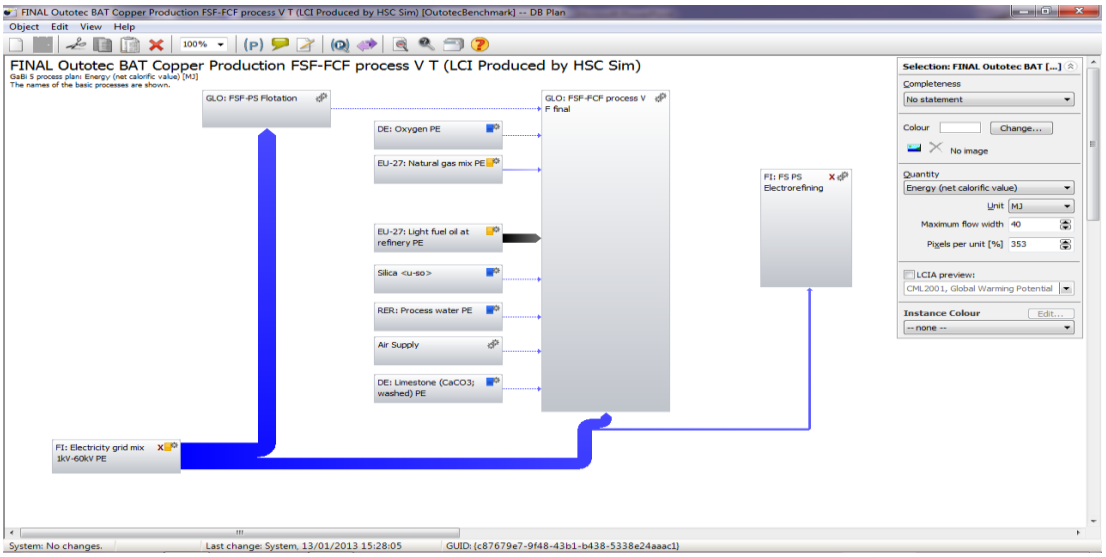


Figure 14, Energy flows of FSF-FCF (Vartiainen) process (GaBi)[33]

The net calorific values of the emissions can be conveniently presented as column in Figure 15.

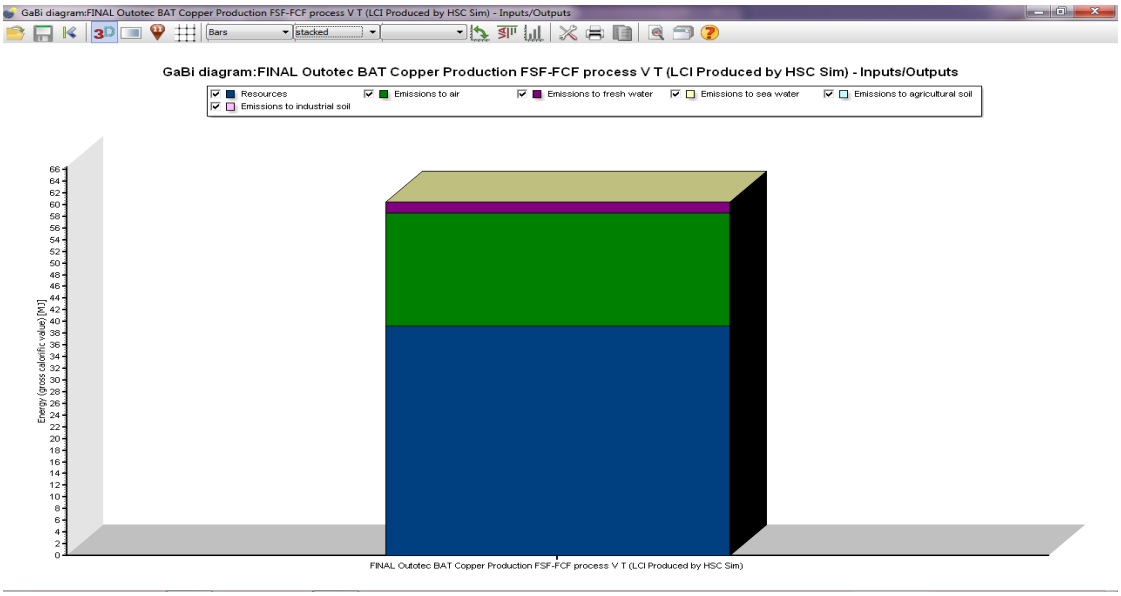


Figure 15, Gross calorific value of the emissions by destination for FSF-FCF (Vartiainen) process (GaBi)[34]

[33] For the present limited simulation model
[34] For the present limited simulation model

As can be noted from the Figure 15 the most significant form of emissions in this FSF-FCF (Vartiainen) process model would seem to be the resources with an approximated calorific losses of 39 MJ/t Cu, while the emissions to air would be equal to losses equaling about 19 MJ/t Cu and emissions to water are approximately equal to 2 MJ/t Cu totalling some 61MJ/t Cu. If the FSF-FCF (Smelter A) case was considered the resource use would be 48 MJ/t Cu while emissions to the air would be 17 MJ/t Cu and emissions to water would equal 2 MJ/t Cu totalling about 67 MJ/t Cu.

Similarly the models for FSF-PS were created and run in GaBi. The results for GWP, AP are shown in the Figure 16.

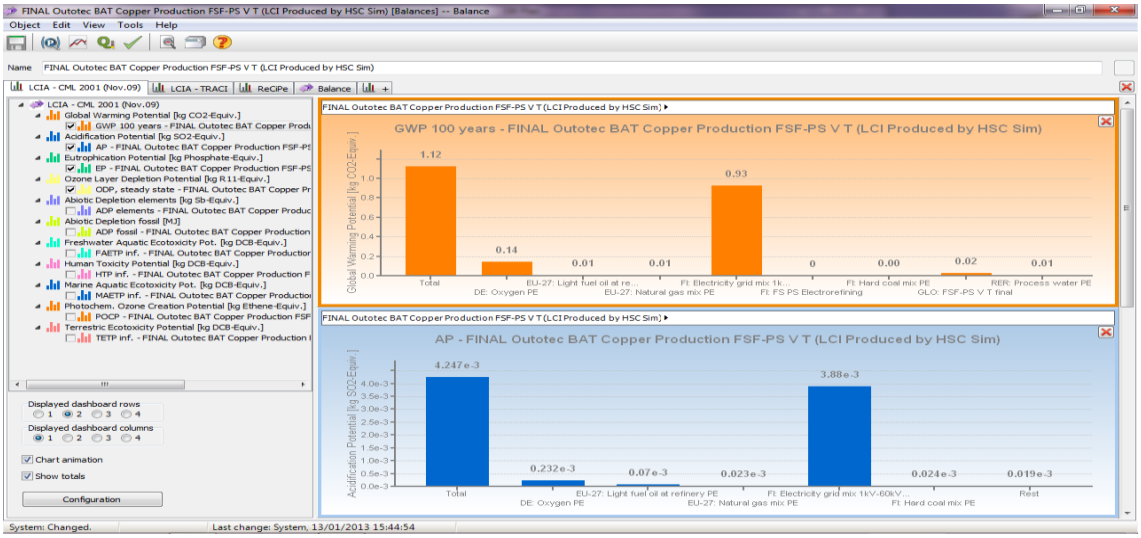


Figure 16, GWP and AP for FSF-PS (Vartiainen) process, GaBi) [35]

Similarly, as for FSF-FCF, the electricity would seem to be contributing significantly to these values. It should be noted here, that as the fugitive emissions of FSF-PS are not included within the model the values might be missing significant data. Thus this is rather a demonstration what can be archived by combining the HSC-Sim ™ data with GaBi.

And for energy flows and source of consumption similar pictures were drawn which are shown in Figure 17 and Figure 18.

[35] For the present limited model

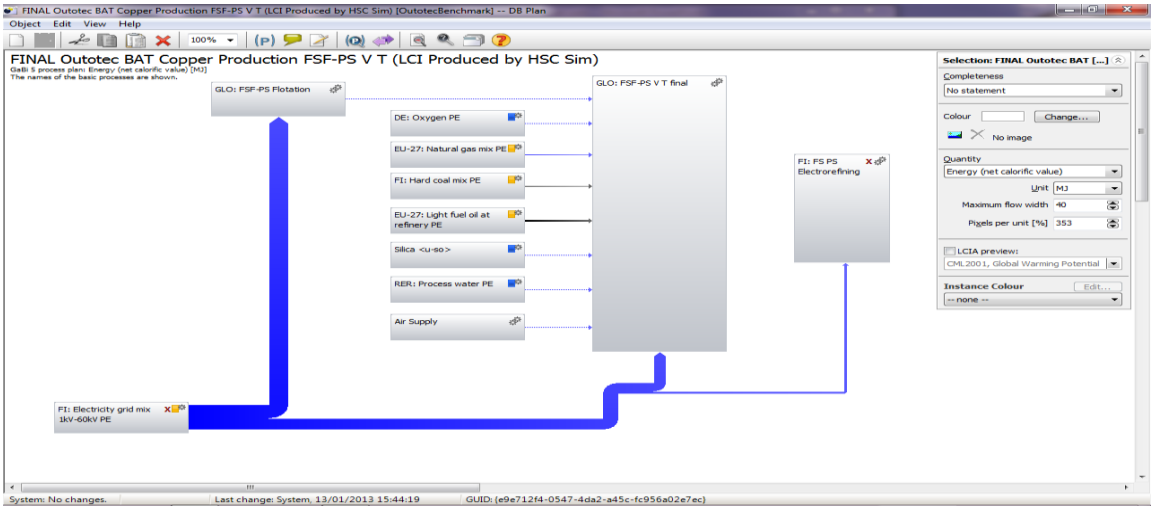


Figure 17, Energy flows of FSF-PS (Vartiainen) in GaBi

It can be easily noted that the electric energy is consumed mostly in the flotation, grinding and Flash Smelter parts of the process while the electrorefinings share is least significant. On the other hand most of the fuels are consumed in the Flash Smelter.

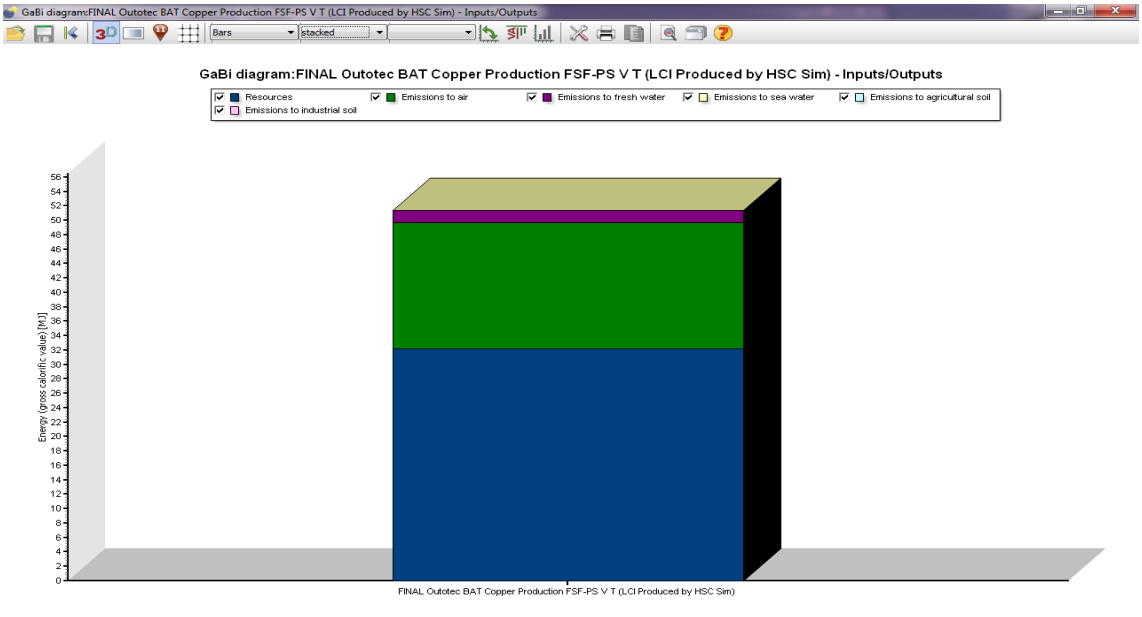


Figure 18, Gross Calorific values of the emissions of FSF-PS (Vartiainen) process by destination (GaBi)

The gross calorific losses in the Figure 18 for FSF-PS (Vartiainen) case would suggest value of 32 MJ/t Cu for resources, 17 MJ/t Cu to air and 2 MJ/t Cu totalling 51 MJ/t Cu. Similar values for FSF-FCF (Smelter A) case would result in 37 MJ/t Cu for resources, 17 MJ/t for emissions in air and about 2 MJ/t to fresh water, totalling some 58 MJ/t Cu.

6.2 Exergetic Life Cycle Assessment (ELCA)

The purpose of ELCA is to define the exergy of inputs and outputs of the system from which the exergetic efficiencies of subsystems as well as the whole system can be calculated. In order to complete this, an inventory analysis is required where the exergies of the input and output flows are defined in detail based on the state of the streams.[36] (R.L.Cornelissen, 1998)

The exergies are calculated based on the production of 1 kg of copper. When electricity is used as utility in the process it is transformed to exergy using ratio 1:1 as the electricity can be perfectly converted to mechanical work (R.U. Ayres, 1996)[37].

As the models were incomplete the results from this part should be considered as preliminary results. For complete assessment the missing parts such as the fugitive emissions and acid plant should be added to the models.

In order to define the exergy consumption of the production system, thermodynamic data for Enthalpy, Entropy and Gibbs energy was required for all the substances and streams of the system in circumstances defined in the model. By using the available database of HSC the exergies of the steams could be calculated by using LCA add-in in HSC-Sim ™.

As the stream data in minerals-mode for flotation flow sheet was based on the distributions rather than the substances the exergy calculations of the flows had to be made by hand. The stream data on the minerals involved to the flotation processes existed within the models which could be used instead for the calculation of exergies.

Proper exergy calculations were available for the flash smelting part of the process as well as for the electrorefining part as the adequate thermodynamic data could be found from the HSC database for these models. In order to analyze the exergy consumption the stream exergies needed to be defined. The exergies for the streams should be calculated using the equations 8 and 12 for the Flash smelter models and equation 11 for electrorefining model represented in the Chapter 3.3.1.

[36] The values represented in this Chapter are based on the best available data.

[37] This approach does not take into account what are the exergetic losses related to the electricity generation as this goes beyond the scope of this thesis.

The exergy losses were calculated first for the process units and then for the whole system as a sum of the exergy losses of the units. To calculate the internal exergy loss of a unit the input and output streams data for the unit were required. By using balance equation for exergy which was defined in R.U. Ayres et al. (1996) paper its possible to write:

$$\boldsymbol{B_{in} = B_{product} + B_{waste} + \Delta B_{process}} \qquad \textbf{Eq. 16}$$

or in this case if the focus was in the internal exergy loss of the unit it can be defined:

$$\boldsymbol{B_{out} = B_{product} + B_{waste}} \qquad \textbf{Eq. 17}$$

and rewritten:

$$\boldsymbol{\Delta B_{process} = B_{in} - B_{out}} \qquad \textbf{Eq. 18}$$

In order to calculate the overall exergy losses, the product exergy needs to be subtracted from the exergy of inputs to get:

$$\boldsymbol{B_{lost} = B_{in} - B_{product} = B_{waste} + \Delta B_{process}} \qquad \textbf{Eq. 19}$$

These are B_{in} = exergy of inputs, $B_{product}$ =exergy of product, B_{waste}=exergy of waste, $\Delta B_{process}$ = internal exergy loss, B_{out} = exergy of outputs, B_{lost} = total exergy loss.

In this Chapter the exergy of fuels that are used externally of the process flows are calculated. The exergy of flows and internal exergy losses of process units for FSF-PS and FSF-FCF flotation and pyrometallurgical processes are introduced as well as the exergies of electrorefining.

6.2.1 Exergy of the External Fuels

In the models external fuels are defined as fuels that are not directly used in the process but rather in heating of streams and other similar purposes. The exergies of fuels were calculated separately for 1 kg of each fuel type using HSC's "mass and balance" property which utilizes equation 8 for the exergy calculations. External fuels that were used in the models were light fuel oil (LFO), Natural gas (NG), Coke (C) and Propane (P). The exergy calculations were based on balance over the system, thus the input and output temperature is 298.15 K. Calculations for LFO are shown in the Table 12 while the results for all other fuels are found in the Table

13[38]. The balance for exergies can be interpreted as the exergy loss which, in fact, is utilized as heat within the processes, except the chemical exergy of the flue gases which is wasted.

Table 12, Exergy values for fuels

Exergy of fuels	[MJ/kg fuel]
LFO	40.80
Coke	8.75
Propane	47.013

Table 13, LFO exergy calculation (HSC)

IN	Amount (kg)	B Ph [MJ]	B Ch (MJ)	B tot (MJ)
Fuel Oil	1	0	42.58	42.58
Air	13.00	0	0.63	0.63
Total	**14.00**	**0**	**43.20**	**43.20**
OUT	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Flue gases	14.00	0	2.40	2.40
Total	**14.00**	**0**	**2.40**	**2.40**
Balance	**0**	**0**	**40.80**	**40.80**

The values for these fuels were utilized later in the Chapters 6.2.3 and 6.2.4 for the external fuel exergies.

6.2.2 Exergy of Electrorefining

The electrorefining is similar for all processes so the results from the electrorefining exergy analysis are applicable in both models and this is why electrorefining is represented first. The product streams were solved by finding a reason for the unit to exist. The rational exergetic efficiencies of the process units are represented in the Table 14.

[38] Exergy calculations for all fuels are found in the Appendix O

Table 14, Exergetic efficiencies of electrorefining process units

Process Unit	Product stream	Rational efficiency
CuER	Cathode	93 %
Crystallization	Solution1, $CuSO_4$	95 %
Cu EW	Impure cathodes	100 %
Cu_3As EW	Cu_3As	33 %
Evaporation	H_2SO_4 70-m-%	74 %
SeAg Prec	CuNi Sol2	95 %
Se Roasting	Se-free slime	56 %
Dore	Dore Anodes	17 %
Leaching	CuNi Sol1	98 %
Te Sementation	CuNi Sol3	95 %
H_2SO_4 division	Acid 90%	90 %
Washing	Washed slime	99 %
Precious metals handling	Metals out	86 %

Most importantly the copper electrorefining has high exergetic efficiency of 93% which has most significance for the electrorefining process. Based on the input and output exergies of streams the exergetic losses for the process units were calculated in the Table 15.

Table 15, Exergetic losses of electrorefining process units

Unit[39]	ΔB Ph [kJ/kg Cu]	ΔB Ch [kJ/kg Cu]	ΔB [kJ/kg Cu]
CuER	-0.88	7.32	**6.44**
Crystallization	1.69	-52.33	**-50.64**
Cu EW	0.00	0.00	**0.00**
Cu_3As EW	0.00	0.00	**0.00**
Evaporation	0.00	0.00	**0.00**
SeAg Prec	0.00	-0.94	**-0.94**
Se Roasting	-0.12	0.89	**0.77**
Dore	-2.21	3.78	**1.57**
Leaching	0.00	-4.34	**-4.34**
Te Cementation	0.00	0.08	**0.08**
H_2SO_4 division	0.00	0.00	**0.00**
Washing	0.09	0.00	**0.09**
Precious metals handling	0.00	0.92	**0.92**
Sum	**-1.42**	**-44.62**	**-46.04**

ΔB Electricity [kJ/kgCu]	972.0
ΔB tot [kJ/kgCu]	**926.0**

[39] This follows the process model's flow sheet unit naming, which is repeated procedure for later lists as well. A complete list of the units for the processes represented can be found in the appendix M.

It can be seen that the actual process has negative exergetic losses unless the exergy of electricity was included. With electricity included the exergetic losses of electrorefining becomes 926.0 kJ/kg Cu. Most significant exergy generation can be found in the Crystallization. It should be noted that the exergies that are involved with crystal formation are ignored in the exergy calculations and thus this is not an exact value for the exergy generation of the process unit.

When the exergies are calculated over the system boundaries the balance is slightly different as can be seen from the Table 16 where the exergies of inputs and outputs are added together at the system boundaries.

Table 16, Exergetic losses of electrorefining at system boundaries

Stream exergies	ΔB Ph	ΔB Ch	ΔB
B In [kJ/kgCu]	976	2852	3828
B Out [kJ/kgCu]	5	2898	2903
ΔB loss [kJ/kgCu]	**971**	**-46**	**925**

The values include also the electricity use, which is taken into account at the physical exergy. As the input exergy was 3828 kJ/kg Cu and output exergy of cathode copper was 2092 kJ/kg this would result in the exergetic efficiency of 54.7% for the electrorefining process. In fact there is the production of precious metals and others but these are such marginal values that these can be ignored for now.

6.2.3 Exergy of FSF-PS Process

In order to calculate the total exergy loss of the FSF-PS process the internal exergy losses were defined at the process units as well as at the system boundaries. The streams are known from the model and the exergies of the streams are calculated in the HSC. The internal exergy losses for the process units in HSC were calculated using equation 18.

The exergy calculations for flotation were based on the mineralogical composition of the flows for which there existed detailed information. The temperature was assumed to be constant 298.15 K so the only factor that needed to be taken into account was the Chemical exergy and the exergy of mixing. As the database values for Sphalerite ((Zn,Fe)S) and Anorthite ($CaAl_2SiO_8$) in HSC didn't exist, some simplifying assumptions were made on the Gibbs free energies of

these substances. For Sphalerite ((Zn,Fe)S) the average values of Gibbs free energies of FeS and ZnS were used to get estimated $\Delta_f G$= -149kJ/mol and for Anorthite ($CaAl_2SiO_8$) the Gibbs free energy of aluminium silicate (Al_2SiO_5) $\Delta_f G$= -2444kJ/mol was used as these two substances had some chemical similarities. The effect of these assumptions is likely rather marginal as the share of one of these minerals was 4.1 m-% at most at any time and the error of the values shouldn't be very large. The exergies of the flotation streams were calculated by using the model data and the exergy values of the minerals that were manually calculated using equation 8 for each mineral[40]. The exergies that are caused by structural elements such as crystals are not taken into account for now.

While analyzing the exergy of flotation process the main focus was the rational efficiency of the process units as the exergetic losses within the process units didn't take place as the chemical and physical exergies were in practice unaltered as the mixing exergies were rather small. Also the exergy difference between input and output of the whole flotation process was of interest as the chemical substances in the streams remained the same.

The total exergetic efficiency of the flotation process was 5.5% as the input ore had an exergy content of 571.1 MJ/kg Cu, which includes the electricity used for grinding. Output Cu concentrate (25 m-%) had exergy value of 31.41 MJ/kg Cu and the rest is exergy losses totaling 539.7 MJ/kg Cu of which most is contained in the ore tailings and a small part in the water.

The approach represented previously for the whole system is not very good for estimating the efficiencies of the process units as the tailing do not have any practical value. If the actual input was considered to be instead the Chalcopyrite $CuFeS_2$ and water a 0-exergy assumption for the ore could be made. Thus the exergies of other than chalcopyrite minerals are not included to the efficiency calculations as the purpose of the unit operations is factually to concentrate the chalcopyrite. An exception is made for grinding where the whole exergy of the stream is taken into account to emphasize the actual exergy losses related to the grinding of the ore. Note in the Table 17 that the electricity is on the output side while the exergy of the feed is on the input side for grinding. For the other units where electricity is used the electricity is added to the input side as physical exergy component while most of the exergy is in water and chalcopyrite. The results from the analysis are shown in the Table 17.

[40] See Appendix N for the exergies of the flotation process streams.

Table 17, Exergetic efficiencies of flotation process units for FSF-PS process

List of Units	Product Stream	Input [kJ/kg Cu]	Output [kJ/kg Cu]	Efficiency
Grinding	FlotationFeed	571259	5945	**1.04 %**
Conditioner	RghFeed	35114	35237	**100.3 %**
Rougher flotation	RghConcentrate	50276	34444	**68.5 %**
Rougher Scavenger	ScavConc	15742	5503	**35.0 %**
Tail Sump	FinalTail	10050	10050	**100.0 %**
TailsThickener	TailsThick.OF	10050	6158	**61.3 %**
ConcentrateThickener	ConcThick.UF	25542	25929	**101.5 %**
PFSump	PFFeed	25929	25929	**100.0 %**
ConCFilter	FinalConcentrate	25929	24566	**94.7 %**
Pond	TailSolids	3892	1280	**32.9 %**
WaterTank	MillWater	9302	9302	**100.0 %**
RghScavConcSump	RghScanConc	39948	39948	**100.0 %**
Clnr1F	Clnr1F	48666	48666	**100.0 %**
Cleaner1	Clnr1C	48784	33911	**69.5 %**
Clnr2F	Clnr2F	40315	40315	**100.0 %**
Cleaner2	Clnr2C	40364	31596	**78.3 %**
Clnr3F	Clnr3F	31596	31596	**100.0 %**
Cleaner3	Clnr3C	31618	25192	**79.7 %**
ConcSump	FinalConcentrate SL	25192	25192	**100.0 %**

It is worth mentioning that the final output of the flotation process is the concentrate. The exergies of flotation can be used to estimate the total exergetic efficiency of the process while the exergetic efficiency of this part isn't representation of the whole FSF-PS process but it should be rather understood as exergetic efficiency of sub-process only. [41]

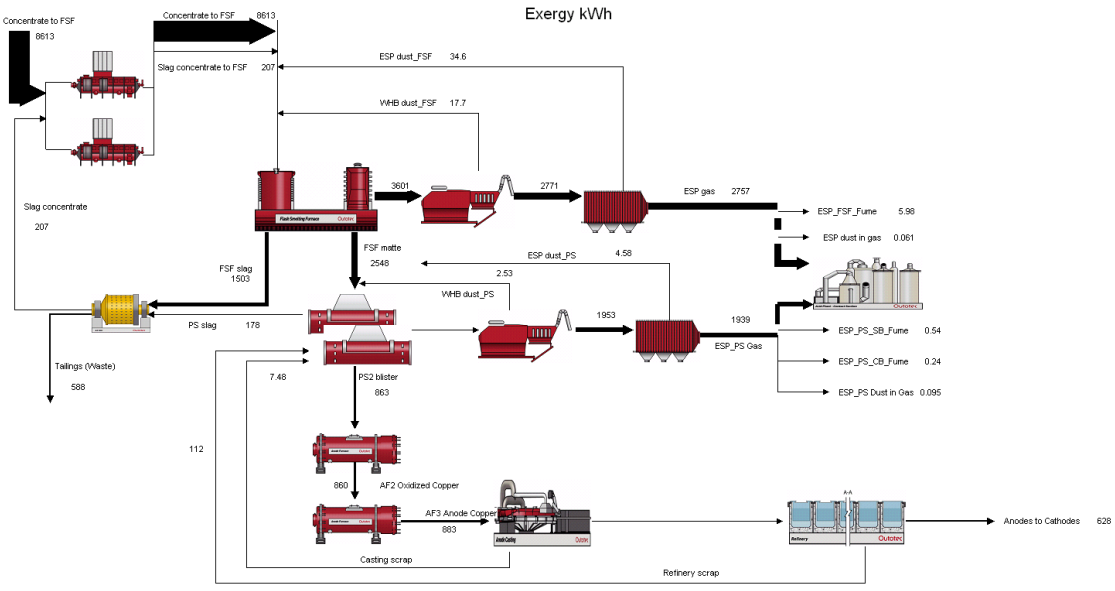
The internal exergy generation of external fuels not directly used in the FSF-PS pyro process is based on the exergy values for "other fuels" in the Tables in the appendix O and amounts and division of external fuels use for FSF-PS process in the Vartiainen report and estimated values for Smelter A. Using this information the values for internal exergy generated in the use of external fuels listed in the Table 18 were calculated.

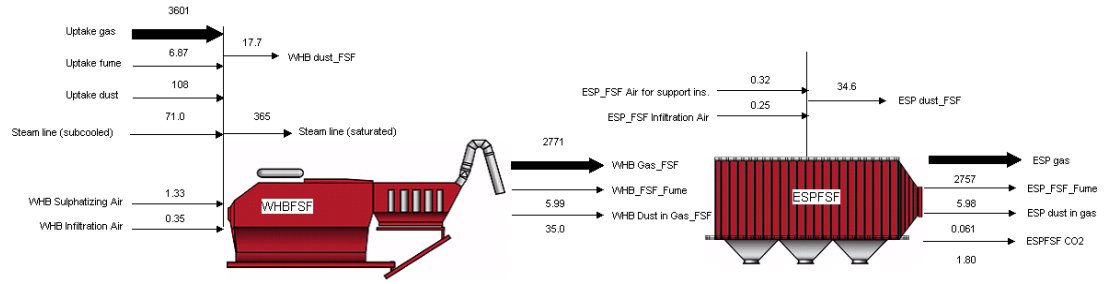
[41] Note also that the surface area related exergy generation is not included to the exergy calculations. This is related mainly to the grinding part of the flotation process and is subject to discussion.

Table 18, Internal exergy losses of external fuels in FSF-PS process

FSF-PS	Smelter A		Vartiainen	
Fuel type	**Amount kg/kg Cu**	**kJ/kg Cu**	**Amount kg/kg Cu**	**kJ/kg Cu**
LFO	0.073	2 973.8	0.024	964.9
Propane	0.048	2 233.3	0.015	724.6
Coke	0.042	368.5	0.014	119.6
Total		**5 575.6**		**1 809.1**

A Sankey –diagram could be used to visualize the exergy flows of the FSF-PS pyro process. The stream exergy values in the Sankey-diagram are originally [kWh/t Cu]. Not all input streams are included to these flow sheets as part of the streams are visible only in in-detail flow sheets.





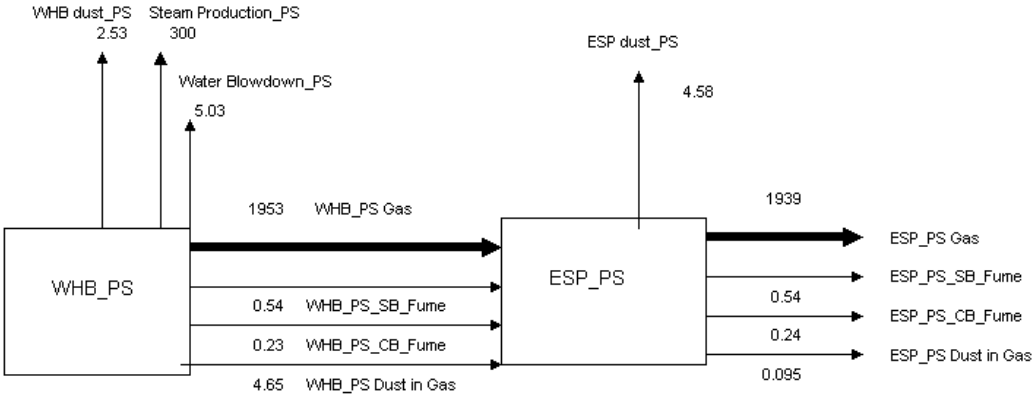


Figure 19, Sankey- diagram of exergy flows of FSF-PS process and off-gas handling

The internal exergy losses for the process units in the Flash smelter of FSF-PS process are found in the Table 19. The exergy losses of external fuels are added separately to the Table values for Smelter A and Vartiainen fuel consumption cases.

Table 19, Internal exergy losses by process unit in Flash smelting in FSF-PS process

FSF-PS Process	ΔB Ph [kJ/kg Cu]	ΔB Ch [kJ/kg Cu]	ΔB process [kJ/kg Cu]
SD1	-61.6	81.5	19.9
SD2	-61.6	81.5	19.9
SD mixer 1	0.0	0.0	0.0
SD mixer 2	26.7	0.0	26.7
FSF	-6739.0	11099.0	4360.0
FSF UP	61.5	18.3	79.8
WHBFSF	2784.0	-647.5	2136.5
ESPFSF	32.3	14.0	46.2
PS_sb	-399.4	927.2	527.8
PS_cb	-891.5	1713.8	822.3
PS_sr	7.8	0.1	7.9
PS_s2af	-0.2	0.0	-0.2
WHB_PS	1133.7	-336.3	797.4
ESP_PS	7.5	19.3	26.8
AFOX	-111.9	208.6	96.7
AFRE	-289.3	-38.8	-328.2
anode handling	486.4	0.0	486.4
SC	2862.8	328.4	3191.3
Total	**-1151.7**	**13468.9**	**12317.2**
Electricity [kJ/kg Cu]	4089.80		
Case	**Smelter A**	**Vartiainen**	
Δ B fuel [kJ/kg Cu]	5575.6	1809.1	
Δ B [kJ/kg Cu]	**21982.6**	**18216.1**	

Most significant chemical exergy losses can be found in the units where heat intensive chemical reactions take place such as Flash Smelting Furnace and PS units while significant losses in physical exergy are found in units with large heat differences such as Waste Heat Boilers or in units that doesn't utilize the heat at all such as the Scavenger.

The units with negative exergies require external fuels to compensate so that the exergy generation becomes positive. Thus the inclusion of external fuels is the next step. Part of the exergy is recovered as is the case for the steam generated at the waste heat boilers that is partly utilized at the steam dryers. For this reason when calculating the efficiencies the steam generation is regarded as a product as can be seen later in this Chapter.

The rational exergetic efficiencies for process units can be calculated using the input exergies together with "main product" stream exergies according to equation 14. The product stream is defined here as the stream that is the reason for the process unit to exist (as we did earlier). As an example the waste heat boiler (WHB) exists to generate steam, thus the steam is the product for such unit. The product streams and exergetic efficiencies are found in the Table 20.

Table 20, Rational exergetic efficiencies of process units for FSF-PS pyro process

Unit name	Product stream	Rational efficiency
FSF	Matte	28.3 %
FSF UP	Flue gas	99.4 %
AFOX	Oxidized Copper	91.8 %
AFRE	Anode Copper	101.0 %
WHBFSF	Steam	11.4 %
ESPFSF	Dust	1.2 %
WHB_PS	Steam	10.7%
ESP_PS	Dust	0.2 %
SD1	Off-Gas	1.0 %
SD2	Off-Gas	1.0 %
SD mixer 1	Concentrate+slag	100.0 %
SD mixer 2	Concentrate+slag	99.9 %
PS_sb	White Metal	73.6 %
PS_cb	Blister	41.4 %
PS_sr	Slag	12.9 %
PS_s2af	Slag to AF	35.0 %
Anode handling	Anode copper	71.1 %
SC	Slag concentrate	12.3 %

The exergy losses were calculated previously by unit but it is informative to represent the exergies at the system boundaries. In the FSF-PS flash smelter model streams with unknown input or output source could be used for this purpose. The input exergy of streams was 32733 kJ/kg Cu while the output exergy of streams was 20461 kJ/kg Cu suggesting a loss of 12272 kJ/kg Cu. The small difference of 0.37% between the exergy losses over units and the system is likely caused by some unknown inconsistencies within the model. The electricity consumption was added as such to the physical exergy while the exergy of external fuels was added to the total chemical exergy. The exergies of inputs and outputs are found in the Table 21.

Table 21, Exergies [kJ/kg Cu] at the system boundaries of FSF-PS flash smelter

Smelter A			
FSF-PS	**B Ph [kJ/kg Cu]**	**B Ch [kJ/kg Cu]**	**B Tot [kJ/kg Cu]**
Input	4416	38030	**42447**
Output	1435	19341	**20777**
Exergy Loss	**2981**	**18689**	**21670**
Vartiainen			
FSF-PS	**B Ph [kJ/kg Cu]**	**B Ch [kJ/kg Cu]**	**B Tot [kJ/kg Cu]**
Input	4416	34366	**38782**
Output	1435	19128	**20564**
Exergy Loss	**2981**	**15238**	**18218**

There are various ways to calculate the exergetic efficiency based on what is understood as the product of the total process. Three cases are calculated for exergetic efficiency where the product changes. The first case was with anode copper as product. The second case was when anode copper, slag, steam and 99.8% of the SO_2 recovery in acid plant were reconsidered as products. Only the exergy of recovered SO_2 is taken into account in this example and the resource consumption related to sulphuric acid plant should be taken into account in later assessments. Third case was when the physical exergies of hot anode copper and slag streams are used instead of cold streams. The product exergies are found in the Table 22.

Table 22, Product exergies for FSF-PS flash smelting process

Product	**Exergy**	
Anode Cu	**2261**	kJ/kg Cu
Anode Cu, slag, steam and SO_2 recovery 99.8%	**19229**	kJ/kg Cu
Hot anode Cu & slag, SO_2, steam	**23009**	kJ/kg Cu
Not hot with fugitive (example)	**18577**	kJ/kg Cu

By using these exergies, together with the input exergies found in the Table 21, the following exergetic efficiencies found in Table 23 for the FSF-PS process could be calculated.

Table 23, Exergetic efficiency of FSF-PS pyro processes

EFFICIENCIES	Smelter A	Vartiainen
Anode Cu	5.3 %	5.8 %
Anode Cu, slag, steam and SO_2 recovery 99.8%	**45.3 %**	**49.6 %**
Hot anode Cu & slag, SO_2, steam	54.2 %	59.3 %
Cu, slag, steam, with 5% SO_2 fugitives (example)	43.8 %	47.9 %

If only Cu was considered as product the efficiencies of the process would be rather low at 5.3-5.8%. In the modern flash smelting processes there are other streams that can be understood as products and these streams can be utilized. The relevant exergetic efficiency is then the option which includes anode Cu, slag, steam and 99.8% recovery of SO_2 as products resulting in efficiencies of 45.3-49.6%. The hot products case on the other hand describes how much the efficiency could be improved if most significant heat sources were utilized as energy, giving a theoretic exergetic efficiency of 54.2-59.3% which is approximation of the maximum efficiency which could be archived without changing the chemistry of the process. If smaller sources of heat were utilized, even higher efficiencies could be possibly archived. The last rows exergetic efficiencies take into account the fugitive emissions when 95% of SO_2 is captured. It should be regarded as a calculation example as the actual fugitive missions were not taken into account in this model.

The exergy losses for the whole system are taken into account (including the electricity to the calculations) in the Table 24 for both cases.

Table 24, Exergy losses for whole FCF-PS process at the system boundaries

FSF-PS (Smelter A)	B Ph [kJ/kg Cu]	B Ch [kJ/kg Cu]	Tot [kJ/kg Cu]
Electrorefining	972	-12	**959**
FSF-PS	2981	18689	**21670**
Flotation FSF-PS	6604	3138	**9742**
Total	**10557**	**21815**	**32372**
FSF-PS (Vartiainen)	**B Ph [kJ/kg Cu]**	**B Ch [kJ/kg Cu]**	**Tot [kJ/kg Cu]**
Electrorefining	972	-12	**959**
FSF-PS	2981	15238	**18218**
Flotation FSF-PS	6604	3138	**9742**
Total	**10557**	**18364**	**28920**

These values should give a fair approximation of the exergy losses of the system. It is worth mentioning that the difference in fuel cases is only visible in the chemical exergies as the addition of external fuels does not have an impact on other exergy values and the electrorefining and flotation processes are the same for FSF-PS regardless of case.

The exergetic efficiencies for the whole process system are represented in the Table 25 in case when the total exergies of inputs are taken into account and in case where zero-exergy assumption is made for bulk of the ore.

Table 25, Total exergetic efficiencies of FSF-PS process

Product	Smelter A	Vartiainen	Unit
Exergy Input	577862	573900	kJ/kg Cu
Exergy Input (zero-exergy for ore)	41741	37761	kJ/kg Cu
Exergy Output, Cathode, steam, SO_2 (99.8%)	19061	19061	kJ/kg Cu
Exergy efficiency	**3.3 %**	**3.3 %**	
Exergy efficiency, (zero-exergy ore)	**45.7 %**	**50.5 %**	

It can be noticed that when the exergy of ore is taken into account the efficiency is significantly lower as compared to the case where the exergy of ore is not taken into account. This has some consequences which will be discussed later in the Chapters 7.2 and 9.

6.2.4 Exergy of FSF-FCF Process

Similar assumptions were made for the flotation part of the FSF-FCF process as for the FSF-PS process. The multiplier for the stream values of FSF-FCF process as compared to FSF-PS values is 1.0071 (=97.83/97.14, calculated using ore feed). As the flotation processes are the same, the rational efficiencies of the process units are the same as for the FSF-PS flotation processes which could be found in the Table 17. The obtained exergetic efficiency of 5.56% is also the same for flotation process. The differences can be found in the exergy values of the flows as FSF-FCF flotation process has slightly higher mass flows as compared to FSF-PS flotation processes. The exergies of inputs and products of the FSF-FCF flotation process are found in the Table 26.

Table 26, Exergy of flows of FSF-FCF flotation process units

List of Units	Product Stream	Input [kJ/kg Cu]	Output Input [kJ/kg Cu]
Grinding	FlotationFeed	575335	5987
Conditioner	RghFeed	35364	35488
Rougher flotation	RghConcentrate	50635	34690
Rougher Scavenger	ScavConc	15854	5543
Tail Sump	FinalTail	10122	10122
TailsThickener	TailsThick. OF	10122	6202
ConcentrateThickener	ConcentrateThick.UF	25724	26114
PFSump	PFFeed	26114	26114
ConCFilter	FinalConcentrate	26114	24741
Pond	TailSolids	3920	1289
WaterTank	MillWater	9368	9368
RghScavConcSump	RghScanConc	40233	40233
Clnr1F	Clnr1F	49013	49013
Cleaner1	Clnr1C	49132	34153
Clnr2F	Clnr2F	40603	40603
Cleaner2	Clnr2C	40652	31822
Clnr3F	Clnr3F	31822	31822
Cleaner3	Clnr3C	31843	25372
ConcSump	FinalConcentrate SL	25372	25372

Where for input exergy of grinding the ore exergy content is taken into account and the electricity is on the output side. The Exergy losses of the FSF-FCF flotation process are 543.5 MJ/kg Cu, while the exergy of the product concentrate is 31.6 MJ/kg Cu as compared to FSF-PS values of 539.7 and 31.4 MJ/kg Cu accordingly if the ore exergy is taken into account.

Similarly as for FSF-PS it was assumed 0-exergy for the ore the same assumption is made here for FSF-FCF. The inputs were then the water, chalcopyrite and electricity and the outputs were the concentrated chalcopyrite. The exergy content of the ore input was 28.5 MJ/kg Cu while the electricity was 6.65 MJ/kg Cu. The output exergy of moisture and chalcopyrite in the concentrate was 25.4 MJ/kg Cu giving an exergetic loss of 9.81MJ/kg Cu. As the processes for FSF-PS and FSF-FCF flotation process are equal, so is the exergetic efficiency of 70.3%. This exergy “loss” is more practical when regarding the efficiency of the process units.

The Exergies for the FSF-FCF flash smelter were calculated similarly (as for the FSF-PS flash smelter) directly from the streams. The external fuel exergies are calculated for FSF-FCF Vartiainen and Smelter A cases in the Table 27.

Table 27, External fuel exergies of FSF-FCF flash smelter process

FSF-FCF	Smelter A		Vartiainen	
Fuel type	**kg/kg Cu**	**kJ/kg Cu**	**kg/kg Cu**	**kJ/kg Cu**
LFO	0.080	3 265.3	0.026	1080.5
Propane	0.041	1 937.0	0.014	641.00
Total		**5 202.3**		**1721.5**

The exergy balances were taken over the process units in order to estimate the exergy losses of these operations. The internal exergy losses for the process units in the Flash smelter are found in the Table 28. The exergy losses of external fuels are added to the Table values for Smelter A and Vartiainen cases using the models and fuel exergy Tables from Chapter 6.2.1.

Table 28, Exergy losses of process units of FSF-FCF process

FSF-FCF process	ΔB Ph [kJ/kg Cu]	ΔB Ch [kJ/kg Cu]	ΔB process [kJ/kg Cu]
SD1	-61.6	81.5	**19.9**
SD2	-61.6	81.5	**19.9**
SD mixer 1	0.0	0.0	**0.0**
SD mixer 2	8.1	0.0	**8.1**
FSF	-6514.5	10757.5	**4242.9**
FSFUP	59.2	20.0	**79.2**
FSF Matte granulation	709.3	38.4	**747.7**
WHBFSF	2335.5	-497.8	**1837.7**
ESPFSF	31.3	13.2	**44.6**
FCF	-1676.4	3140.6	**1464.2**
FCF_UP	28.1	15.9	**44.1**
FCF slag granulation	261.1	52.4	**313.6**
WHB_FCF	825.2	-86.8	**738.4**
ESP_FCF	11.8	63.0	**74.8**
AFOX	-298.1	542.5	**244.3**
AFRE	-293.8	-33.0	**-326.7**
Anode handling	490.1	0.0	**490.1**
SC	2936.5	332.1	**3268.6**
Total	**-1209.5**	**14520.9**	**13311.4**
Electricity [kJ/kg Cu]	**4137.8**		
Case	**Smelter A**	**Vartiainen**	
Δ B fuel [kJ/kg Cu]	**5202.3**	**1721.5**	
Δ B [kJ/kg Cu]	**22651.5**	**19170.8**	

A Sankey- diagram for the FSF-FCF process can be drawn by using the HSC-Sim ™.

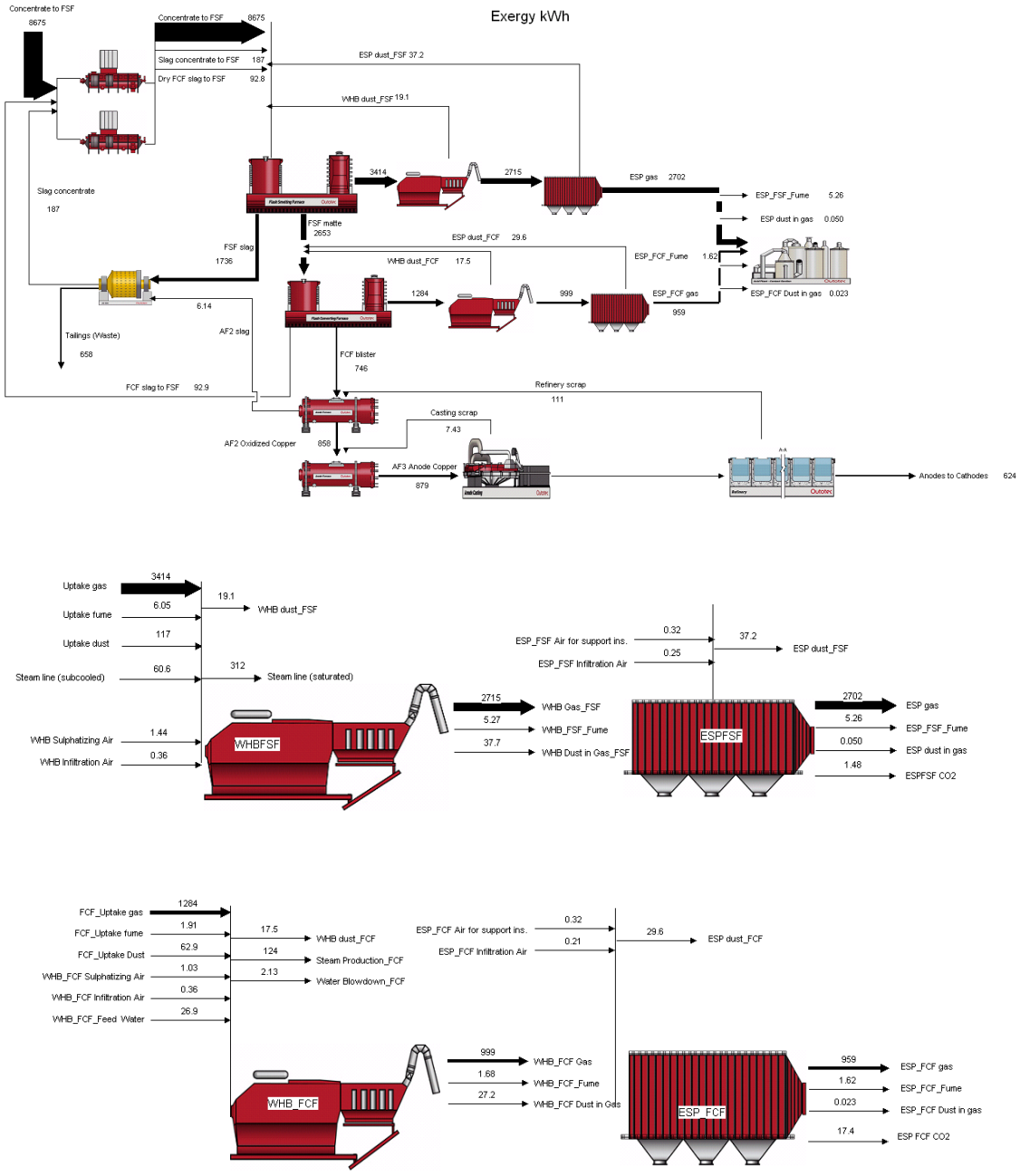


Figure 20, Sankey-diagram of exergy flows of FSF-FCF process

If the balance is taken over system boundaries the exergy of the material inflows to the FSF-FCF process are 35766 kJ/kg Cu (not including the fuels) while the outflow exergy is equal to 22429 kJ/kg Cu which would suggest internal exergy losses worth 13336 kJ/kg Cu. Now if the fuels and electricity are taken into account the values change according to the Table 29

Table 29, Exergy losses of FSF-FCF flash smelter process at the system boundaries

Smelter A			
FSF-FCF	**B Ph [kJ/kg Cu]**	**B Ch [kJ/kg Cu]**	**B Tot [kJ/kg Cu]**
Input	4384	40968	45352
Output	1522	21202	22724
Exergy Loss	**2862**	**19766**	**22628**
Vartiainen			
FSF-FCF	**B Ph [kJ/kg Cu]**	**B Ch [kJ/kg Cu]**	**B Tot [kJ/kg Cu]**
Input	4384	37291	41674
Output	1522	21005	22527
Exergy Loss	**2862**	**16285**	**19148**

The differences between these exergy losses and the losses when the balance is taken over the units are marginal 0.1-0.12% which might be caused by some inconsistencies within the model.

Depending on the definition of the "product" the exergetic efficiency of the FSF-FCF process can be evaluated when same definitions of products were used as for FSF-PS process[42]. For this purpose the exergies of the alternative products are represented in the Table 30.

Table 30, Product exergies of FSF-FCF process flash smelter

Product	**Exergy**	**Unit**
Anode Cu	**2248**	kJ/ kg Cu
Anode Cu, slag, steam and SO_2 recovery 99.8%	**18965**	kJ/ kg Cu
Hot anode Cu & slag, SO_2, steam	**22819**	kJ/ kg Cu

By using these exergies together with the input exergies found in the Table 29 the following exergetic efficiencies for the FSF-FCF process flash smelter could be calculated.

Table 31, Exergetic efficiency of FSF-FCF process flash smelter

EFFICIENCIES	**Smelter A**	**Vartiainen**
Anode Cu	5.0 %	5.4 %
Anode Cu, slag, steam and SO_2 recovery 99.8%	**41.8 %**	**45.5 %**
Hot anode Cu & slag, SO_2, steam	50.3 %	54.8 %

The relevant efficiencies for the processes are those where Cu, slag, steam and SO_2 recovery of 99.8% are taken as products. The exergetic efficiency of the process would in that case be

[42] see pages 86-87

41.8-45.5%. The last rows efficiencies suggest the theoretical maximum efficiency of 50.3-54.8% in case if the heat of most significant hot streams physical exergies could be utilized, such as the hot anodes and slag. A complete model would give appropriate results so these are rather preliminary than decisive results.

The exergy losses over the whole system for FSF-FCF process are found in the Table 32:

Table 32, Exergy lossess of FSF-FCF process

FSF-FCF (Smelter A)	B Ph [kJ/kg Cu]	B Ch [kJ/kg Cu]	B Tot [kJ/kg Cu]
Electrorefining	972	-12	959
FSF-FCF	2862	19766	22628
Flotation FSF-FCF	6651	3161	9812
Total	**10485**	**22914**	**33400**
FSF-FCF (Vartiainen)	**B Ph [kJ/kg Cu]**	**B Ch [kJ/kg Cu]**	**B Tot [kJ/kg Cu]**
Electrorefining	972	-12	959
FSF-FCF	2862	16285	19148
Flotation FSF-PS	6651	3161	9812
Total	**10485**	**19434**	**29919**

If the exergetic efficiencies were taken over the whole copper production system the exergetic efficiencies for FSF-FCF would differ according to the calculation assumptions. In the Table 33 the exergetic efficiencies in case when the total exergy is taken into account and in case if zero-exergy assumption was made are represented.

Table 33, Total exergetic efficiencies of FSF-FCF process

FSF-FCF process	Smelter A	Vartiainen	Unit
Exergy Input	584311	580633	kJ/kg Cu
Exergy Input (zero-exergy ore)	41724	38046	kJ/kg Cu
Exergy Output, Cathode, steam, SO_2 (99.8%)	18965	18965	kJ/kg Cu
Exergy efficiency	**3.2 %**	**3.3 %**	
Exergy efficiency, (zero-exergy ore)	**45.5 %**	**49.8 %**	

7 Conclusions

Some non-definitive conclusions due to the model restrictions are drawn in this Chapter. In Chapter 7.1 the connectivity of the programs and questions related to energy, LCA and GaBi are discussed. In Chapter 7.2 the exergies of the processes are discussed. In Chapter 7.3 the synthesis of the LCA and exergy is made.

7.1 Energy and GaBi

The connection of HSC models within the GaBi was a success and complete environmental data for the system was easily accessible as the inventory analysis was rather simple as the models required only some adjustments so as to complete the system.

The energy consumption based on the calculations for FSF-FCF smelter was 7.32-10.66 GJ/t Cu and for FSF-PS smelter the energy consumption was 6.17-9.96 GJ/t Cu, while for the whole process the values were 14.95-18.28 GJ/t Cu and 13.75-17.53 GJ/t Cu accordingly when the existing models were examined. The energy consumption variation in this case is likely caused by the possible differences in the reference concentrate grades[43] which affect the external fuel needs due to increased stream heating need. The inclusion of external fuels and electricity were an important part of the LCA, as these had rather large significance for the GWP values in the form of CO_2 generated in the burning of fossil fuels for generation of electricity as well as for heat. The processes released small amounts of SO_2 to the atmosphere as such as most of the SO_2 was captured in the models for further use and no fugitive emissions were taken into account. According to the values from GaBi the electricity production seems to be the most significant source for SO_2 as well as CO_2 and equivalent emissions. The inclusion of missing acid plant and fugitive emissions would likely have an effect on these values. Most significantly the inclusion of fugitive emissions could affect significantly the Acidification Potential (AP) of the FSF-PS process.

The HSC-Sim ™ connection with GaBi allowed an easily accessible and usable tool that proved that more accurate LCA's can be archived and should be considered as an addition to current average based values in order to obtain even more accurate results. Besides this the LCA add-in together with exergy calculation scheme in HSC-Sim ™ allowed way to perform exergy

[43] as Vartiainen case and Smelter A case might not have the same concentrate grade, this could explain the variation in the external fuel consumption values.

assessment automatically that could increase the use of ELCA in connection to LCA. In an ideal world all the production systems of the world could be assessed so as to revert from the use of averages to the use of real values which then could be collected to a common database.

7.2 Exergy

Its better start by taking a closer look at the exergetic losses of the process units for both processes as has been done in the Figures 21 and 22. It should be mentioned that the electricity and external fuels are not included to these values, as no unit specific data were possible to apply here and thus the exergy data is slightly incomplete.

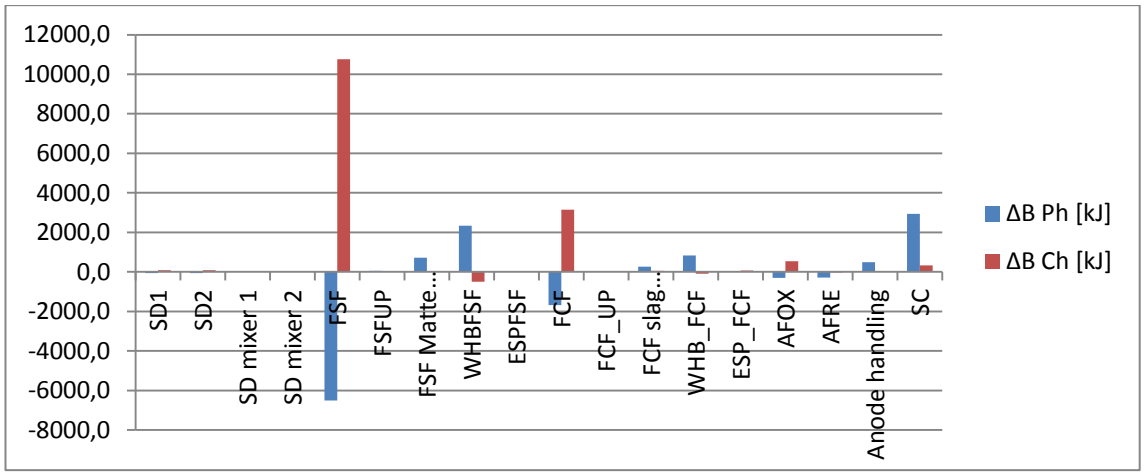


Figure 21, FSF-FCF unit is chemical and physical exergy losses

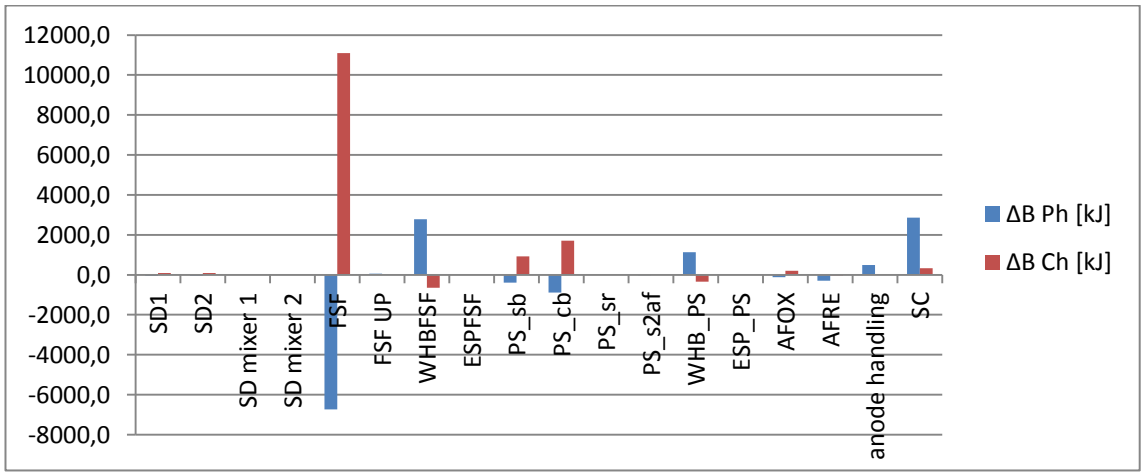


Figure 22, FSF-PS unit is chemical and physical exergy losses

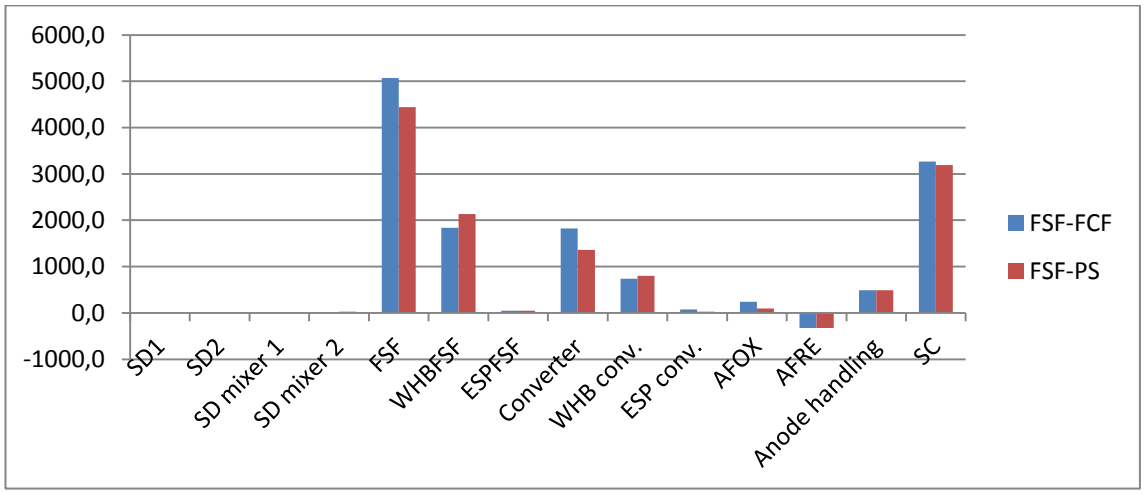


Figure 23, Comparison of unit exergy losses of FSF-FCF and FSF-PS processes

The exergy losses of waste heat boilers are caused mainly by the poor exergetic efficiency of heat recovery as the quality of heat as source for exergy generation is low. As the off gas streams exergy losses are almost equal in size the waste heat boilers do not actually contribute to the difference significantly. Part of the difference in exergies can be explained by the need of matte granulation while the rest can be explained by the differences between the Flash Converting Furnace and Peirce-Smith converter.

The utilized FCF-PS off-gas SO_2 has an exergy content of 13032 kJ/kg Cu while utilized FSF-FCF off-gas SO_2 has exergy content of 12672 kJ/kg Cu giving a difference of 360 kJ/kg Cu on the product side. The granulation of matte in FSF-FCF process increases the FSF-FCF flash smelter process exergetic losses by 748 kJ/kg Cu, mainly physical exergy losses, as the matte temperature after granulation is 25C and needs to be reheated.

It is possible that the exergy of off-gas SO_2 in FSF-FCF process can be recovered more efficiently than the exergy of SO_2 in FSF-PS process due to higher concentrations of SO_2 in the off-gas which lowers the energy and resource demand of the acid plant for FSF-FCF process. Besides this the FSF-FCF smelter is practically a closed system as compared to FSF-PS smelter from which fugitive emissions are released at the end of the batch process.

As the processes are analyzed it becomes clear that the most significant for exergetic efficiency improvement in smelters is the recovery of the stream heat, which is also the most difficult to archive. FSF-PS flash smelting model exergetic efficiency could be improved by 8.7-9.7% (19.7

% in relative terms) at most while the FSF-FCF flash smelter could be improved by 8.5-9.2% (20.3 % in relative terms) similarly by utilizing better the physical exergies related to heat differences between the streams and reference state. For further exergetic efficiency improvements the chemistry of the process would require changes.[44]

When the total exergetic efficiencies are compared for the whole process it becomes clear that the processes are practically similar in the exergetic efficiency with efficiency of 3.2-3.3%, when the ore exergy is taken into account. When zero assumption is made for the ore, the exergetic efficiency for FSF-FCF process becomes 45.5-49.8% and for FSF-PS process 45.7-50.5%. These values are within the error margins of the model. Here a conclusion can be made that if the grinded ore was utilized the exergetic losses could be reduced significantly when the exergy of ore is taken into account. On the other hand if the zero-exergy assumption was made the exergetic efficiencies could be then improved mainly through the process improvements such as the heat recovery of the slag and anode copper which was discussed previously.

The energy consumption suggested in this Thesis seems to be somewhat in line with L. Landner and L. Lindeström (1999) values for the smelter. If the mass flows and electricity consumption are compared to R.U. Ayres and A. Masini (1996) Figure 3 it can be noted that the mass values of input and output of the smelter process are very similar, while the fuel consumption is lower as compared to their values. As compared to the exergy values, the exergy losses obtained here (28.9-33.4GJ/t) seem to be slightly larger as compared to R.U. Ayres and A. Masini (1996) value of 26.2 GJ/t for the whole process even though the steel balls & rods and explosives are not taken into account in this study. On the other hand the estimations made by L. Landner and L. Lindeström (1999) would suggest exergy losses for smelter and refining process as low as 7.3 GJ/t for modernized flash smelter and 38.7 GJ/t for whole process. It is hard to define where the difference between these two studies comes from as the details are not known for R.U. Ayres and A. Masini (1996) nor L. Landner and L. Lindeström (1999) study. As the differences are compared to literature, it seems that the main difference comes from the flash smelter. It is likely that the differences arises as in the models presented here the steam and water are not always in the reference temperature of 25 ^{o}C but instead these streams might have rather significant temperatures (due to possibly closed

[44] These results are for incomplete model and will likely change as the complete model is represented.

water circuit) giving way for physical exergy losses as well as there are some differences in the way the exergies are calculated for FSF processes as for this part no zero-exergy assumption is made. These assumption possibly increases the exergetic losses for the models represented here.

7.3 Synthesis of Exergy and Energy

To complete the analysis, energy and exergy consumption should be analyzed together. If a closer look is taken on the energy use and efficiencies some phenomenon appears.

Starting from the concentration it is evident that the crushing of the ore is highly inefficient (1.04 %) as only a fraction of the electricity (exergy) consumption is actually directed on the crushing of chalcopyrite while rest is spent on crushing non-valuable ores or on friction. The flotation and cleaning of the ore on the other hand are rather energy and exergy efficient unit operations. In these operations most of the chemical exergy (61.3-79.7%) is actually recovered from the copper containing minerals (chalcopyrite) as those are floating at the surface of the tanks and collected with relatively small electricity input.

When the flash smelter energy and exergy consumptions are analyzed it is necessary to exclude the external fuels and external electricity consumption when analyzing the unit operations as there didn't exist that detailed data on the allocation of the consumption of these utilities.

It can be noticed that on the units where most of the exergy is lost in the form of chemical exergy (such as FSF with exergetic efficiencies of 19.0-28.3%) the exergetic efficiencies are higher as compared to the units where the physical exergy is lost in the form of heat (such as WHB with exergetic efficiencies of 8.7-11.4%, depending on the unit), while the units where electricity is used the exergetic efficiencies are typically highest (such as the electrorefining[45]). This relates to the question of the quality of the energy source. The chemical energy that is connected to the exothermic reactions and oxidation, such as fuel oils or chalcopyrite can be utilized (in general) more efficiently as compared to the physical energy related to the heat which would require significantly lower heat differences in order for the exergy to be utilized efficiently. Most of all the electricity is generally the highest quality energy.

[45]The grinding is an exception.

Then it shouldn't be a surprise, that the electrorefining is then most exergy efficient process with efficiency of 93 % according to results and 93-98 % for current efficiency (G. Davenport, 2011), which does not take into account the sources of energy consumption. According to the LCA the electricity consumption is one of the most significant sources for many of the environmental indicators.

The most important question related the electricity generation is then: what is the source of the energy in electricity generation? Typical sources for electricity production are non-renewable fuels, such as coal, natural gas or fuel oil (chemical exergy) and nuclear fuels (physical exergy), or renewable resources, such as the water, wind or sun light (physical exergy). The use of electricity in Flash-smelting is then more of a question of the energy generation source, which is beyond the scope of this research.

Another thing that was related to the exergetic efficiencies was the mass flows and how much of the flow was separated as product and how much is separated for other purposes. In some process units the actual product mass flow is marginal as compared to the total flow, as in the electrostatic precipitators or steam dryers where large masses are treated while only small fraction is removed, which lowers the rational efficiency significantly. If the heat was recovered and utilized more efficiently, then the exergetic efficiency could be significantly higher.

8 Discussion and Recommendations

The use of HSC-Sim ™ data made it accessible to have more accurate LCA's than previously when the data acquired from the HSC-Sim ™ was connected to GaBi data base. Besides this the HSC-Sim ™ exergy calculation scheme made it possible to perform Exergetic Life Cycle Assessment easily which in addition to LCA gives useful information regarding the use of resources.

It can be seen from the preliminary results that theoretically over 10% efficiency improvement (in absolute terms) could be archived if the physical exergy of hot streams was possible to capture in full. In reality the large temperature differences between the molten slag or anode copper and any possible coolant fluid are such great in value that the heat recovery exergetic efficiencies are expected to be low as the heat transfer coefficient is dependent of the heat difference between the coolant and the hot fluid as the equation 20 shows.

$$U = \frac{Q}{A\Delta T_m} \qquad 20$$

Where, U=heat transfer coefficient, Q= heat flow, A=heat transfer area, ΔT=logarithmic temperature difference.

Despite of this challenge at least some part of the physical exergy currently lost could be captured from the hot anodes and slag in form of steam and possibly electricity for example by spraying water on the anodes in a closed system and simultaneously generating high pressure steam as the water would instantly vaporize, which could be possibly utilized for electricity production and/or heat generation. The technical questions and applicability related to such process would require further discussion.

A conclusion on which technology is better can't be based on these results as such and more complete model is required for both processes with proper data on fugitive emissions and acid plant.

For the improvement of the exergy analysis accuracy the electricity use of all process units should be included to the model. This has been accomplished at some level in the Vartiainen (1998) report but the HSC-Sim ™ models didn't have the power feed included to the units. Besides this the Vartiainen (1998) report had a different approach on process units, which

made the applying of electricity and fuel consumption from the report impractical in detailed level for the model units represented here.

If the electricity input, which is required for separation of substance from the main stream, was used instead and only the products exergy input and output were considered, thus making zero-exergy assumption for rest of the flow, another kind of efficiencies would occur but as there didn't exist that detailed data on the energy consumption, for e.g. electrostatic precipitators, such efficiency approach couldn't be applied. Thus for more detailed energy and exergy analysis exact electricity and fuel consumption data is required for the units. The inclusion of some exergy calculation methods to the HSC program are required for more accurate exergy calculations, such as the crystal/area formation related exergies and the exergy of ideal and non-ideal mixing, which is under development.

The inclusion of the acid plant model to the system could be really crucial in the future to get more accurate results for the process models. Also the fugitive emissions would likely make a difference.

Later on the inclusion of the copper use and recycling processes to the system model would be valuable as this would allow more detailed information about the flows and exergy related to anthropogenic copper.

By completing the detailed models for other competing technologies the comparison between the technologies would become easier and the differences in exergetic efficiencies between the technologies could provide important information and opportunities for process improvements as well it would be important for defining the BAT.

When making the investment decisions and to complete the environmental approach an addition of a Strategic Environmental Assessment (SEA) would be required taking into account the LCA and ELCA that can provide information on the developments in the resource use of the processes in the future (Finnveden et al., 2003). Besides this the economic approach is required to judge the plant profitability. An addition of the economical element to the model could provide more information on the feasibility of the process as well as the profitability of the plant and investments should be made based on all of these factors. A proper tool for assessing the environmental (including the exergy) and economic impacts should be considered.

9 Summary

The purpose of this Thesis was to utilize new simulation tools in order to establish a framework for performing life cycle assessment and and exergy analysis for copper production process. The connection between the HSC-Sim ™ and GaBi programs was established through the LCA mapping tool in HSC-Sim ™ which made it possible to perform an accurate LCA in GaBi.

In the literature part the environmental impact methods such as LCA and exergy were discussed in detail and the calculation schemes for exergy were introduced. The Copper production and use were introduced in general level and the hydro- and pyrometallurgical processes were presented as well as the copper use in society.

The experimental part of this Thesis involved two simulation programs HSC-Sim ™ and GaBi, of which more attention was paid on the HSC-Sim ™. In experimental part the most evident bugs of HSC-Sim ™'s LCA tool were solved and corrections to the exergy calculation scheme of HSC-Sim ™ were suggested in order to be able to perform exergy analysis for the Flash Smelting Furnace with Flash Converter and Flash Smelting Furnace with Peirce-Smith Converter processes. The simulation models were then introduced for which there existed proper models that were obtained from Outotec. The models that were introduced included flotation model, two pyrometallurgical (FSF-FCF and FSF-PS) models and electrorefining model. The models were adjusted so that the flows from ore to cathode copper were correct and the system boundaries were defined.

The results part included the preliminary LCA and ELCA. The resource consumption of the processes was represented together with the energy consumption. Based on these values Life Cycle Impact Assessment was performed using the GaBi for which some of the results were represented as a demonstration for collaboration between HSC-Sim ™ and GaBi databases. This part of Thesis was based on best available data and it is not complete for which reason the preliminary results from LCIA are only shortly introduced.

In addition to the LCA preliminary Exergetic Life Cycle Assessment was performed based on the models provided, where the exergy losses of the process units were presented as such and for which the electricity and external fuels consumption were added as a bulk value. As the provided models missed the fugitive emissions and the resources related to the acid plant no

final conclusions could be made. Preliminary results were introduced based on the uncomplete models as a demonstration of the functionality of the exergy calculation scheme of the HSC-Sim ™ as well as the LCA-add-in. According to the simulations and calculations based on the provided models, the electrorefining consumed 1.0 MJ/kg Cu exergy, the FSF-PS smelter consumed 18.2-22.0 MJ/kg Cu while FSF-FCF smelter consumed 19.2-22.6 MJ/kg Cu and the flotation consumed 9.7-9.8 MJ/kg when zero-exergy assumption was made for the flotation. The total exergy consumption of FSF-PS process was 28.9-32.7 MJ/kg while the total exergy consumption of FSF-FCF process was 29.8-33.4 MJ/kg Cu. The exergetic efficiencies of the processes varied based on the definition of the efficiency from 3.2-3.3 % for rational efficiency to 45.5-50.5% for rational efficiency and zero-exergy assumption for ore.

It wasn't possible to make any conclusions on the technologies due to some significant limitations (most importantly the Acid plant and fugitive emissions), thus more complete process models will be required to get more specific results. None the less, the preliminary results and methods represented here should be useful for further studies.

The demonstration shows that connection of HSC-Sim ™ and GaBi can be used for performing accurate LCA's. The results of this Thesis also proves that the LCA-add of HSC-Sim ™ and exergy calculation scheme of HSC-Sim ™ can be easily used for performing Exergetic Life Cycle Assessment.

The exergy calculation scheme of HSC-Sim ™ will require improvement so that most importantly the exergy of ideal and non-ideal mixing will be taken into account. Also the exergies related to area formation should be considered as part of the exergy calculation scheme.

10 References

Arpaci, E. and Vendura, T., “Recycling of industrial copper materials”, VDI report (917), Association of German Engineers (VDI), Berlin, 1992.

Arpaci, E, Vendura, T., “Recycling of Copper Materials--Classical and New Procedure of Recovery”, Metall (Germany), Vol. 47, no. 4, Apr. 1993, pp. 340-345.

Ayres, R.U., Ayres, L.W., Martinàs, K., “Eco-thermodynamics: exergy and Life Cycle Analysis”, 96/19/EPS, INSEAD Working Paper Series, 1996, pp. 1-57.

Ayres, R.U., Ayres, L.W., Masini, A., 2006a, “An Application of Exergy Accounting to Five Metals”, Eco-Efficiency in Industry and Science, 19 (2006), pp 141-194.

Ayres, R.U., von Gleich, A., Gößling-Reisemann, S., 2006b, *Sustainable Metals Management, Securing our Future - Steps towards a Closed Loop Economy*, edit. von Gleich, A. , Eco-Efficiency in Industry and Science, 19 (2006), ISBN-10: 1402040075.

Ayres, R.U., Ayres, L.W., Råde, I., “The Life Cycle of Copper, its Co-Products and By-Products”, Mining, Minerals and Sustainable Development, IIED, No. 24, 2002, pp. 1-210.

Bare, J., “Life cycle impact assessment research developments and needs”, Clean Technology Environmental Policy, 12 (2010), pp. 341–351.

Bilgen, S. and Kaygusuz, K., “Thermodynamic Aspects of Renewable and Sustainable Development”, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 31 (2009), Issue 4, pp. 287-298.

Biswas, A., Davenport, W.G., *Extractive metallurgy of copper*, 3rd edition, 1994, Elsevier Science Press, New York, ISBN-10: 0080421245.

Brodyansky, V.M., Sorin, M.V., Le Goff, P., *The efficiency of industrial processes: Exergy analysis and optimization,* Elsevier, Amsterdam, 1994, ISBN-10: 0444899960.

Brown, T.J. , Walters, A.S., Idoine, N.E., Shaw, R.A., Wrighton, C.E., Bide, T., 2012, "World Mineral Production 2006-10", British Geological Survey, Nottingham, UK,

Burkin, A.R., *Chemical Hydrometallurgy – Theory and Principles*, Imperial College Press, London, 2001, ISBN-10: 1860941842.

Castro, M.B.G., Remmerswaal, J.A.M., Boin, U., and Reuter, M.A., "A thermodynamic approach to the compatibility of materials combinations for recycling", Resources, Conservation and Recycling, 43 (2005) No. 1, pp. 1-20.

Castro, M.B.G., Remmerswaal, J.A.M., Brezet, J.C., Reuter, M.A., "Exergy losses during recycling and the resource efficiency of product systems", Resources, Conservation and Recycling, 52 (2007), pp. 219–233.

Cornelissen, R.L., "*Thermodynamics and Sustainable Development: The use of Exergy Analysis and the Reduction of Irreversibility",* Doctoral Thesis under supervision of G.G Hirs and T.J Kotas, Twente University, Netherlands, 1998.

Cornelissen, R.L., Hirs, G.G., "The value of the exergetic life cycle assessment besides the LCA", Energy Conversion and Management, 43 (2002), pp.1417–1424.

Dincer, I. and Rosen, M.A., *"Exergy-Energy, Environment and Sustainable Development"*, Elsevier, 2007, ISBN 978-0-08-044529-8.

Davenport, W.G., King, M.J., Schlesinger, M.E., Biswas, A.K., *Extractive Metallurgy of Copper*, 4th edition (2002), Pergamon, ISBN: 0-08-044029-0.

Davenport, W.G, King, M.J., Schlesinger, M.E., Sole, K.C., 2011, Extractive Metallurgy of Copper, 5th edition, Pergamon, ISBN: 978-0-08-096789-9.

Dewitt, T.W., Graig, A.B. jr, 1980, "Control of Copper Smelter Fugitive Emissions", Environmental Protection Agency (EPA), available at: http://nepis.epa.gov/Exe/ZyNET.exe/91014LHH.txt?ZyActionD=ZyDocument&Client=EPA&Index=1976%20Thru%201980&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&UseQField=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C76THRU80%5CTXT%5C00000023%5C91014LHH.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=p%7Cf&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=10&ZyEntry=1 (visited 31.1.2013)

Edelstein, D., "Minerals Yearbook: Copper", USGS, Washington, D.C, 1999.

Finnveden, G., Nilsson, M., Johansson, J., Persson, Å., Moberg, Å., Carlsson, T., "Strategic Environmental Assessment Methodologies—Applications Within the Energy Sector", Environmental Impact Assessment Review, 23 (2003), pp. 91–123

Finnveden, G., Östlund, P., "Exergies of Natural Resources in Life-Cycle Assessment and Other Applications", Energy, 22 (1997), No. 9, pp. 923-931.

Giurco, D., Stewart, M., Suljada, T., Petrie, J., 2006, "Copper Recycling Alternatives: An Environmental Analysis", Working Paper, 5th Annual Environmental Engineering Research Event, 20–23 October 2006, Noosa, QLD.

Graedel, T.E., Allwood, J., Birat, J.-P., Reck, B.K., Sibley, S.F., Sonnemann, G., Buchert, M., Hagelüken, C., "Recycling Rates of Metals – A Status Report, A Report of the Working Group on the Global Metal Flows to the International Resource Panel", UNEP (2011), available at http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metals_Recycling_Rates_110412-1.pdf (visited 22.8.2012)

Graedel, T.E., van Beers, D., Bertram, M., Fuse, K., Gordon, R.B., Gritsinin, A., Kapur, A., Klee, R.J., Lifset, R.J., Memon, L., Rechberger, H., Spatari, S. and Vexler, D., 2004, "Multilevel Cycle of Anthropogenic Copper", Environmental Science & Technology, 38 (2004), issue 4, pp. 1242-1252. [UNEP reference]

Guinee, J., Heijungs, R., Huppes, G., Zamagni, A., Masoni, P., Buonamici, R., Ekvall, T., Rydberg, T., "Life Cycle Assessment Past, Present, and Future", Environmental. Science Technology, 45 (2011), pp. 90–96.

Gößling-Reisemann, S., "*Entropy as a measure for resource consumption - Application to primary and secondary copper production*", In: Gleich, A. von; Ayres, R. U.; Gößling-Reisemann, S., "*Sustainable Metals Management, Securing our Future - Steps towards a Closed Loop Economy"*, Eco-efficiency in industry and science, 19 (2006), pp. 195–236.

Gößling-Reisemann, S., "Entropy analysis of metal production and recycling", Management of Environmental Quality: An International Journal, 19 (2008), No. 4, 2008, pp. 487-492.

International Copper Study Group (ICSG), "The World Copper Fact Book", 2010, available at: http://www.scribd.com/doc/52153185/41/Global-Copper-Recyclables-Use-2002-2008 (visited 17.8.2012)

International Energy Association (IEA), "Tracking Industrial Energy Efficiency and CO_2 emissions", Energy Indicators, 2007, available at: http://www.iea.org/publications/freepublications/publication/tracking_emissions.pdf (visited 9.1.2013)

International Finance Group (IFG), "Pollution Prevention and Abatement Handbook", WORLD BANK GROUP, Effective July 1998, available at: http://www1.ifc.org/wps/wcm/connect/45bb400048865823b456f66a6515bb18/copper_PPAH.pdf?MOD=AJPERES (Visited 11.3.2013)

Jolly, J.L.W., "The US copper-base scrap industry and its byproducts: an overview", United States Geological Survey (USGS), July 23, 1999.

Laukkanen, T., Järvinen, M. and Fogelholm, C.-J., "Introduction to Exergy Analysis - Including useful examples", Aalto University, Espoo, 15 March 2011.

Lossin, A., "Copper", Ullmann's Encyclopedia of Industrial Chemistry, 10 (2012), pp. 163-222, Hamburg, Germany, DOI:10.1002/14356007.a07_471.

Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., *IPCC Special Report on Carbon dioxide Capture and Storage*, Chapter 3, International Panel for Climate Change (IPCC), 2005, pp.105-178, ISBN-10: 0-521-68551-6, available at http://www.ipcc.ch/pdf/special-reports/srccs/srccs_Chapter3.pdf (visited 28.1.2013)

Najdenov, I., Raic, K.T., Kokeza, G., "Aspects of Energy reduction by Autogenously Copper Production in the Copper Smelting Plant Bor", Energy, 43 (2012), Issue 1, July 2012.

Norgate, T., Jahanshahi, S., "Energy and Greenhouse Gas Implications of Deteriorating Quality Ore Reserves", conference paper, 5th Australian Conference on Life Cycle Assesment, Melbourne, 22-24 November 2006.

Pennington, D.W. (a), Rebitzer, G., Ekvall, T., Frischknecht, R., Hunkeler, D., Norris, G., Rydberg, T., Schmidt, W.-P., Suh, S., Weidema, B.P., "Life cycle assessment Part 1: Framework, goal and scope definition, inventory analysis, and application", Environment International, 30 (2004), pp. 701– 720.

Pennington, D.W. (b), Potting, J., Finnveden, G., Lindeijerd, E., Jolliete, O., Rydberg, T., Rebitzere, G., "Life cycle assessment Part 2: Current impact assessment practice", Environment International, 30 (2004), pp. 721– 739.

Risopatron, C.R.,"The Case of Copper", paper presented at Eurometaux Workshop on Metall Recycling Data, Bruxelles, 4 June 2009, [referenced in UNEP]

Roine, A., Mansikka-aho, J., Kotiranta, T., Björklund, P., Lamberg, P., *HSC 7 Manual* (2009), Outotec Oyj, Espoo.

Royal Society of Chemistry (RSC), "Environment, Health and Safety Committee Note on: Life Cycle Assessment", Burlington House, Piccadilly, London, 2012, available at http://www.rsc.org/images/LCA_20100215_tcm18-97943.pdf (visited 20.11.2012)

Sibley, S.F., Buttermann, W.C., staff, "Metals recycling in the United States", Resources, Conservation and Recycling, 15 (1995), Issues 3–4, December 1995, pp. 259–267.

Simada, M., Katagiri, N., Maeda, S., "Supply and consumption of copper in Japan", Paper presented at International Copper Study Group, Lisbon, Portugal, November 1999.

Singer, D.A., and Menzie, W.D., *Quantitative mineral resource assessments —An integrated approach*, Oxford, United Kingdom, Oxford University Press (2010), ISBN-10: 0195399595

Szargut, J., *Exergy Method: Technical and Ecological Applications*, WIT Press (April 12, 2005), ISBN: 978-1-85312-753-3.

Szargut, J., Morris, D.R. and Steward, F.R., *Exergy analysis of thermal, chemical, and metallurgical processes*, Hemisphere Publishing Corporation (31 May 1988), ISBN-10: 0891165746.

Tsatsaronis, G., "Thermoeconomic analysis and optimization of energy systems", Prog. Energy Combust. Sci., 19 (1993), pp. 227-257.

Tsatsaronis, G., "Definitions and Nomenclature in exergy analysis and exergoeconomics" Energy, 32 (2007), pp. 249–253.

Tucker, A., "Life Cycle Assessment as a Tool in Environmental Impact Assessment", Environmental Impact Assessment Review, 20 (2000), pp. 435–456.

Van Beers, D., Bertram, M., Fuse, K., Spatari, S., and Graedel, T. E., “The contemporary African copper cycle: one year stocks and flows”, Journal of the Southern African Institute of Mining and Metallurgy, 93 (2003), pp. 147 – 162.

Vexler, D., Bertram, M., Kapur, A., Spatari, S., and Graedel, T. E., “The contemporary Latin American and Caribbean copper cycle: 1 year stocks and flows”, Resources Conservation and Recycling, 41 (2004), pp. 23 – 46.

Zeltner, C., Bader, H.-P., Scheidegger, R., Baccini, P., “Sustainable metal management exemplified by copper in the USA.”, Reg. Environ. Change, 1 (1999), pp. 31–46.

11 Appendixes

11.1 Appendix A, Copper Minerals

Mineral	Formula	Copper, wt %	Crystal system	Density, g/cm^3
Native copper	Cu	≦99.92	cubic	8.9
Chalcocite	Cu_2S	79.9	orthorhombic	5.5 – 5.8
Digenite	Cu_9S_5	78.0	cubic	5.6
Covellite	CuS	66.5	hexagonal	4.7
Chalcopyrite	$CuFeS_2$	34.6	tetragonal	4.1 – 4.3
Bornite	Cu_5FeS_4/Cu_3FeS_3	55.5 – 69.7	tetragonal	4.9 – 5.3
Tennantite	$Cu_{12}As_4S_{13}$	42 – 52	cubic	4.4 – 4.8
Tetraedrite	$Cu_{12}Sb_4S_{13}$	30 – 45	cubic	4.6 – 5.1
Enargite	Cu_3AsS_4	48.4	orthorhombic	4.4 – 4.5
Bournonite	$CuPbSbS_3$	13.0	orthorhombic	5.7 – 5.9
Cuprite	Cu_2O	88.8	cubic	6.15
Tenorite	CuO	79.9	monoclinic	6.4
Malachite	$CuCO_3 \cdot Cu(OH)_2$	57.5	monoclinic	4.0
Azurite	$2\,CuCO_3 \cdot Cu(OH)_2$	55.3	monoclinic	3.8
Chrysocolla	$CuSiO_3 \cdot n\,H_2O$	30 – 36	(amorphous)	1.9 – 2.3
Dioptase	$Cu_6[Si_6O_{18}] \cdot 6\,H_2O$	40.3	rhombohedral	3.3
Brochantite	$CuSO_4 \cdot 3\,Cu(OH)_2$	56.2	monoclinic	4.0
Antlerite	$CuSO_4 \cdot 2\,Cu(OH)_2$	53.8	orthorhombic	3.9
Chalcanthite	$CuSO_4 \cdot 5\,H_2O$	25.5	triclinic	2.2 – 2.3
Atacamite	$CuCl_2 \cdot 3\,Cu(OH)_2$	59.5	orthorhombic	3.75

(A. Lossin 2012, Table 6, p. 170)

11.2 Appendix B, Smelting

Flash Smelting

In flash smelting the dry Cu-concentrate is dropped from the top of reactor with added silica and oxygen blown to it. The sulphide minerals react with oxygen generating enough heat[46] to melt the minerals that drop at the bottom where sulphide rich matte and oxide rich slag forms at the settling area.

Following exogenous reactions (for chalcopyrite, pyrite and chalcocite accordingly) occur in molten concentrate increasing the temperatures to above 1200 C:

$$CuFeS_2 + \frac{5}{2}O_2 \rightarrow Cu + FeO + 2SO_2 \qquad \Delta H = -720kJ\ (1200\,^{\circ}C) \qquad 21$$

$$FeS_2 + O_2 \rightarrow FeO + 2\,SO_2 \qquad \Delta H = -686kJ\ (1200\,^{\circ}C) \qquad 22$$

$$Cu_2S + 0_2 \rightarrow 2Cu + SO_2 \qquad \Delta H = -216kJ\ (1200\,^{\circ}C) \qquad 23$$

These reactions are enough to provide sufficient heat to enable autogenous operation.

A problem in more traditional copper smelting processes arises as under oxidizing conditions, Cu_2S tends to form Cu_2O. The problem with reaction 4 is that oxidized copper will dissolve to slag and is lost or it needs to be re-concentrated from the slag at a cost.:

$$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2 \qquad \Delta H = -405kJ\ (1200\,^{\circ}C) \qquad 24$$

This problem is controlled by oxidizing most of the iron and by adding some silicate SiO_2 as flux that affects equilibrium compositions. Adding silica to melts creates two separable phases: iron and other oxides together with silica forms a slag while iron and other sulphides form a matte. SiO_2 addition increases on the other hand heating need of the melt thus increasing energy consumption. The higher activity of iron for oxidation reaction compared to copper in the melt enables the separation of most of the iron to the slag and copper to matte. This reaction in unbalanced form can be described as:

$$CuFeS_2 + O_2 + SiO_2 \rightarrow (Cu, Fe, S) + FeO \cdot SiO_2 + SO_2 \qquad 25$$

[46] See the enthalpy values next to reactions

SiO_2 addition also increases slag viscosity as SiO_2 forms polyions in the melt. To control the increased viscosity of the melt due to polyionic silica addition some calcium or magnesium oxide is usually added which disturbs polyion formation, lowering the viscosity. (G. Davenport, 2011)

Another important reaction that can be problematic in smelting is:

$$FeO + Cu_2S \leftrightarrow FeS + Cu_2O \qquad \Delta H = 104kJ\ (1200\,^{\circ}C) \qquad 26$$

This reaction can occur when the FeO activity in the melt is too high as in case if too much of iron is oxidized (too much oxygen in input). The problem with this reaction is that it increases copper concentration in the slag. On the other hand the reverse of this reaction will increase copper content in the slag in the settling area of the furnace. The activity of FeO can also be controlled by adding silica to the melt. (G. Davenport, 2011)

This reaction is described as follows:

$$FeO + SiO_2 \rightarrow FeO - SiO_2 \qquad \Delta H = 29kJ\ (1200\,^{\circ}C) \qquad 27$$

None the less, most problematic reaction for matte and slag formation is the creation of Fe_3O_4 (magnetite):

$$3FeO(l) + 0.5\,O_2(g) \rightarrow Fe_3O_4(s) \qquad \Delta H = -350kJ\ (1200\,^{\circ}C) \qquad 28$$

$$FeO\ (l) + Fe_2O_3(l) \rightarrow Fe_3O_4(s) \qquad \Delta H = -33kJ\ (1200\,^{\circ}C) \qquad 29$$

Magnetite has melting point of 1591 C. It is solid in the smelting temperatures and thus it can cause process barriers by forming a solid layer on the furnaces increasing the external heating need of furnace or by distracting the settling of matte and slag. To manage magnetite formation the oxide and sulphur partial pressures must be controlled to find optimal furnace operation conditions where only small amounts of magnetite are allowed to form. (A. Lossin, 2012, G. Davenport, 2011)

We could conclude that in traditional copper smelting few things needs to be controlled: nitrogen inflow for temperature control; oxygen inflow for temperature control (reaction heat), appropriate melt composition as oxygen inflow is affecting copper oxidization and loss in slag and FeO activity and thus magnetite formation; concentrate composition for constant operating conditions (reactions and equilibrium composition); fossil fuels burning rate for

constant operating conditions (temperature); silica inflow for FeO activity control and for creation of matte and slag phases, CaO or MgO inflow for viscosity control; SO_2 outflow for constant operating conditions for sulphur acid plant (indicates also changes in the melt composition).

Direct-to-Blister Copper

Alternatively Flash furnace and converter could be combined in single furnace as in Outotec's Direct-to-Blister technology that has benefits in capital and operating costs, energy consumption and SO_2 collection but has some disadvantages in copper recovery efficiency within the furnace. (G. Davenport, 2011)

In direct-to-copper furnaces that are operated at 1300 C the following reactions are noTable:

$$2Cu_2O + Cu_2S \xrightarrow[\sim 1300\ C]{} 6Cu + SO_2 \qquad \Delta H = 27kJ\ (1300\,^{\circ}C) \qquad 30$$

$$2Fe_3O_4\ (s) + 2CuS\ (s) \xrightarrow[\sim 1300C]{} 2Cu(l) + FeO\ (l) + SO_2(g)$$

$$\Delta H = 499kJ\ (1300\,^{\circ}C) \qquad 31$$

The high Cu slag (12-28%), as a result of avoiding matte formation (and foaming caused by reaction 3), is separately treated in electric furnaces in direct-to-copper technology with added coke to reduce the oxidized copper. NoTable reactions of coke occurring in slag refining are:

$$Cu_2O(l) + C(s) \xrightarrow[\sim 1300\ C]{} 2Cu(l) + CO(g) \qquad 32$$

$$Fe_3O_4(l,s) + C \xrightarrow[\sim 1300\ C]{} 3FeO(l) + CO(g) \qquad 33$$

$$FeO(l) + C \xrightarrow[\sim 1300]{} Fe(l) + CO(g) \qquad 34$$

This process is most suitable for copper ores that produces little slag such as covellite (Cu_2S) and bornite (Cu_5FeS_4) as the slag reprocessing is costly.

Top Submerged Lance (TSL) Smelting

Another alternative is Top Submerged Lance smelting (Ausmelt/Isasmelt[47]) where the feed is moist concentrate instead of dry concentrate and oxidizing reactions happen within the bath where oxygen is blown through a special lance. It requires external heat mainly from burning

[47] See Appendix E for Ausmelt furnace

of fossil fuels, usually coal that is added to the feed. The coal addition has two purposes in furnace: to generate heat and to reduce CuO in the slag according to reaction:

$$\mathbf{CuO(l) + C(s) \rightarrow Cu(l) + CO(g)} \quad \mathbf{35}$$

Since the reactions happen within the bath the reaction mechanism is expected to be slightly different from flash furnace.

The most important reactions for Ausmelt/Isasmelt copper production are expected to be:

$$\mathbf{6CuFeS_2 + 18Fe_3O_4 \rightarrow 54FeO + 7SO_2 + 3Cu_2S + 2FeS + 4FeO} \quad \mathbf{36}$$

$$\mathbf{54FeO + 9O_2 \rightarrow Fe_3O_4} \quad \mathbf{37}$$

Where $\mathbf{Fe_3O_4}$ would thus function as catalyst instead of process barrier as in other processes. This technology could be used for matte converting as well. In converting, some additional oxygen could be added to the input together with small amount of coal. (G. Davenport, 2011)

Copper Converting and Fire Refining

The matte is collected from furnace for converter in liquid (Peirce-Smith converter[48]) or solid and crushed form (Outotec flash converter[49]) where some more silica (Peirce-Smith) or CaO (Outotec) is added and oxygen is blown through the melt. Oxygen blow oxidizes mainly the sulphur and iron (due to irons higher activity towards oxygen compared to copper) according to the reactions:

$$\mathbf{FeS(l) + 1.5\ O_2(g) \rightarrow FeO\ (l) + SO_2(g)} \quad \mathbf{38}$$

$$\mathbf{3FeS(l) + 5O_2(g) \rightarrow Fe_3O_4 + 3SO_2(g)} \quad \mathbf{39}$$

The iron forms slag with silica or CaO. After iron content of matte is reduced to 1% the slag is collected for recycle to previous furnace while the sulphur in Cu_2S is oxygenized according to reactions:

$$\mathbf{Cu_2S(l) + 1.5O_2(g) \rightarrow Cu_2O(l) + SO_2(g)} \quad \mathbf{40}$$

$$\mathbf{Cu_2S(l) + 2Cu_2O(l) \rightarrow 6Cu(l) + SO_2(g)} \quad \mathbf{41}$$

$$\mathbf{Cu_2S + 0_2 \rightarrow 2Cu\ +\ SO_2} \quad \mathbf{42}$$

[48] See Appendix F for Pierce-Smith converter
[49] See Appendix G For Outotec flash converter

Blister copper, where sulphur content is 0.001-0.03% and oxygen content is 0.1-0.8%, is formed (G. Davenport, 2011).

The blister copper is fire refined using O_2 and hydrocarbon fuels in either rotary refining furnaces or Hearth furnace to remove rest of the oxygen and sulphur dissolved to copper. The oxygen reacts:

$$[S] + O_2(g) \rightarrow SO_2(g) \quad (43)$$

$$O_2(g) \rightarrow 2[O] \quad (44)$$

While the hydrocarbons reduce dissolved oxide as:

$$H_2C(s,l,g) + 2[O] \rightarrow H_2O(g) + CO(g) \quad (45)$$

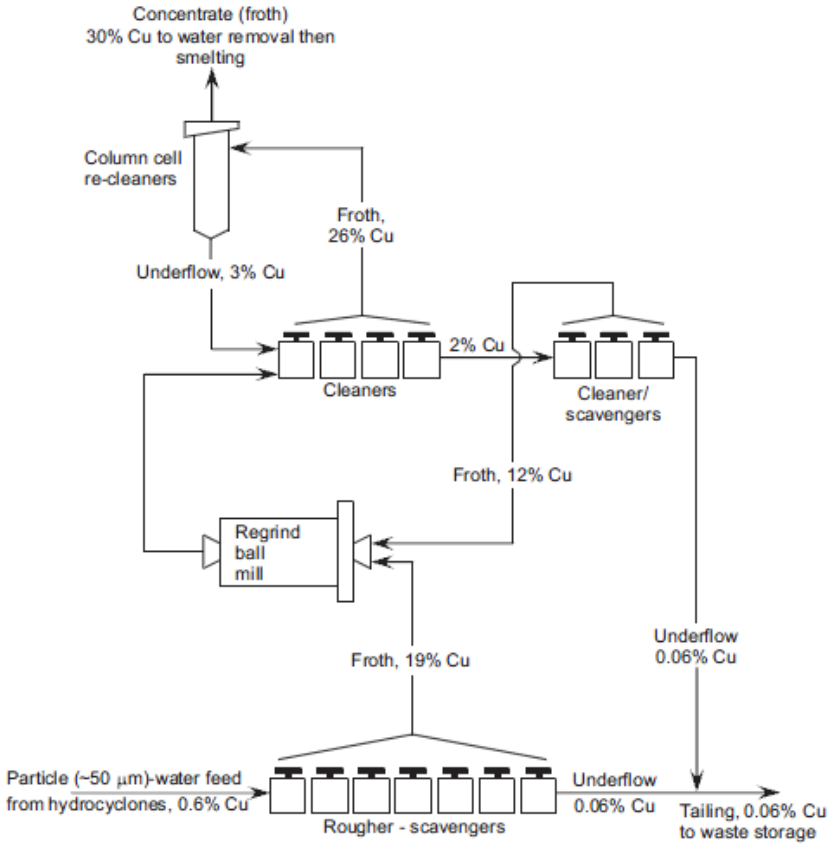
$$CO(g) + [O] \rightarrow CO_2(g) \quad (46)$$

$$H_2(g) + [O] \rightarrow H_2O(g) \quad (47)$$

The blister copper is sent to be cast to anodes and the anodes are sent to electrorefining where it is electrolytically[50] purified to high grade copper (99,999%).

[50] See Appendix H for Electrorefining

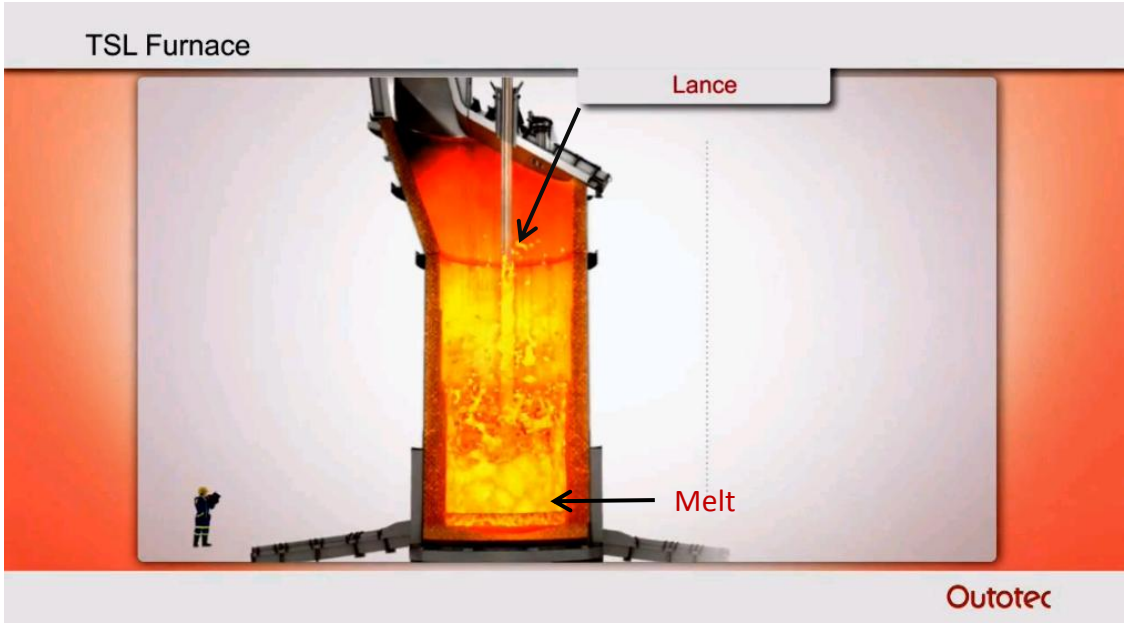
11.3 Appendix C, Froth Flotation Flow Sheet



Producing 30% Cu concentrate from grinded ore with 0.6% Cu

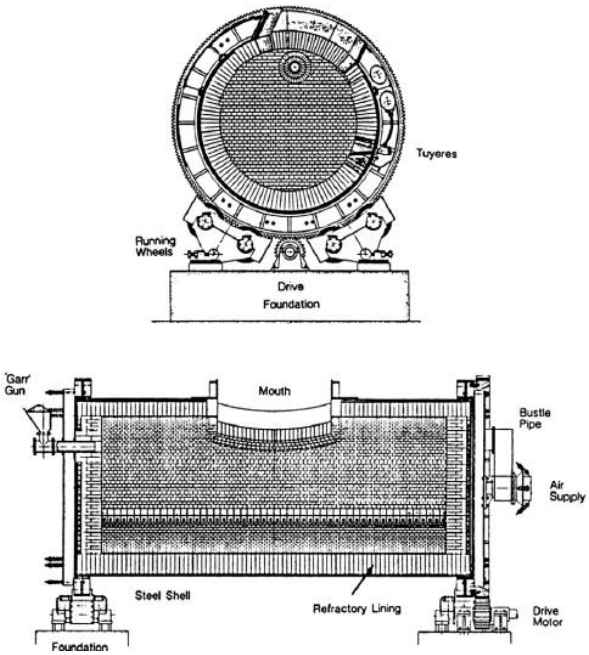
(G. Davenport, 2011, fig 4.3, p. 53)

11.4 Appendix E, Ausmelt Furnace

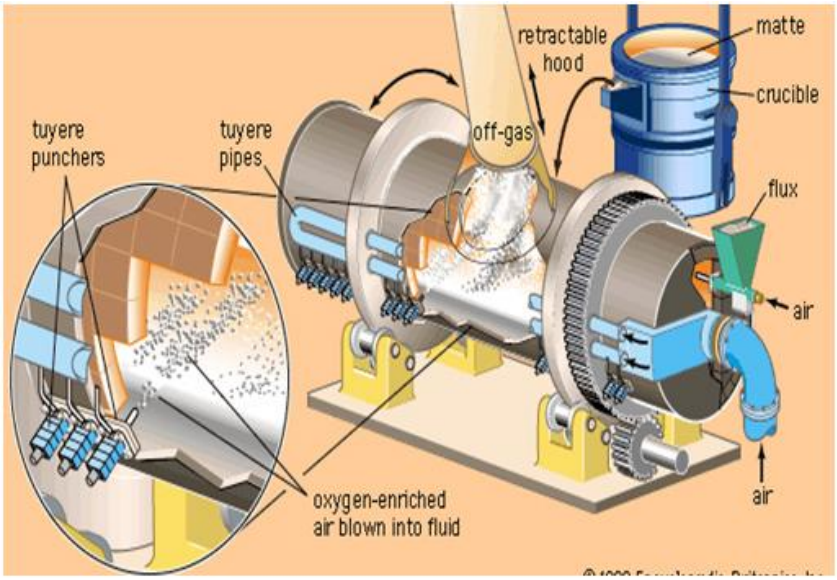


Ausmelt Furnace, Outotec, picture captured from video available at http://www.outotec.com/pages/Page____39927.aspx?epslanguage=EN (visited 28.11.2012) with some additions.

11.5 Appendix F, Pierce-Smith Converter

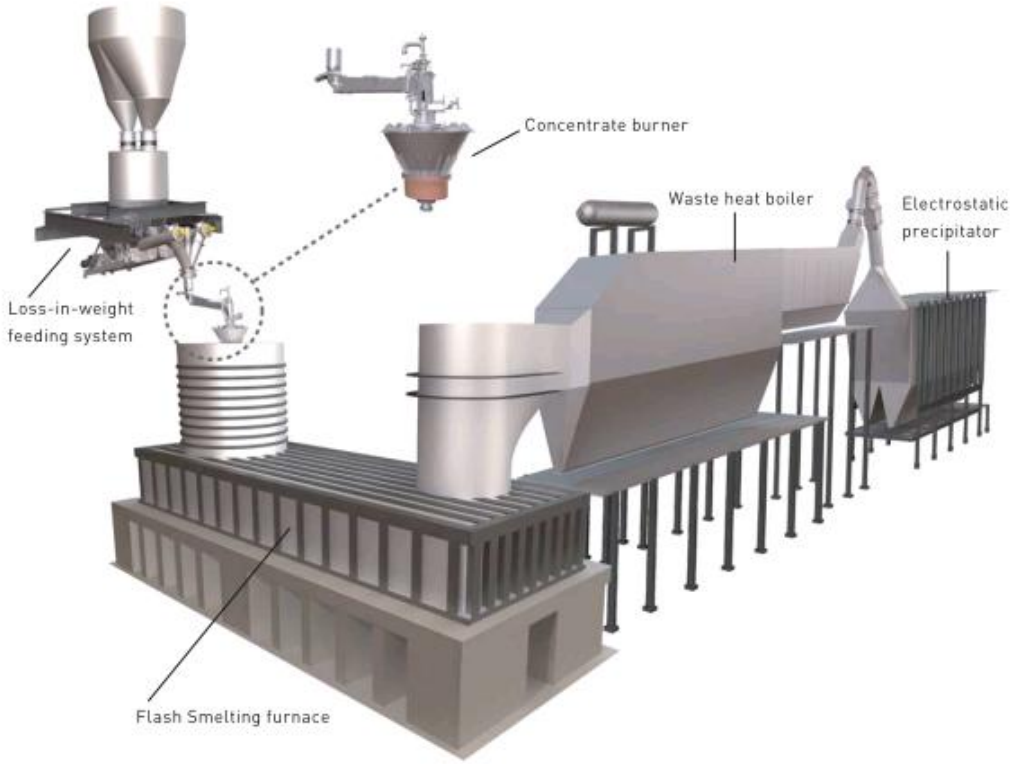


(G. Davenport, 2011, Fig 8.1. p. 128)



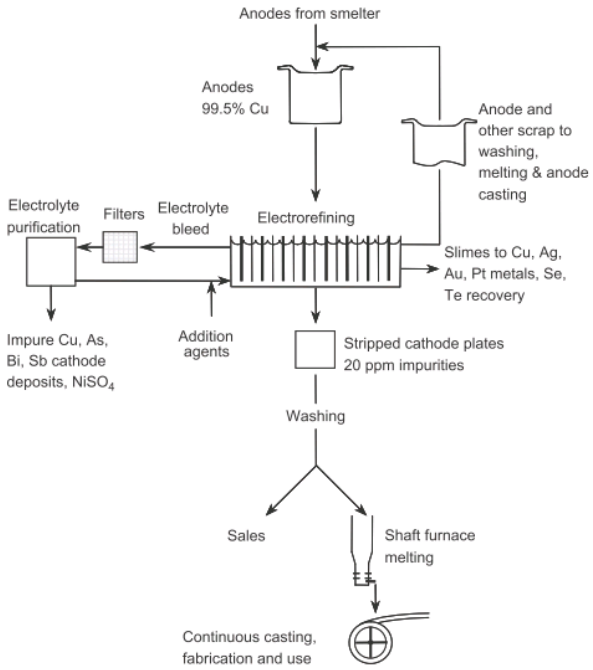
http://www.dundeeprecious.com/English/operations/processing/tsumeb-smelter/smelting/default.aspx (visited 24.1.2013)

11.6 Appendix G, Outotec Flash Furnace

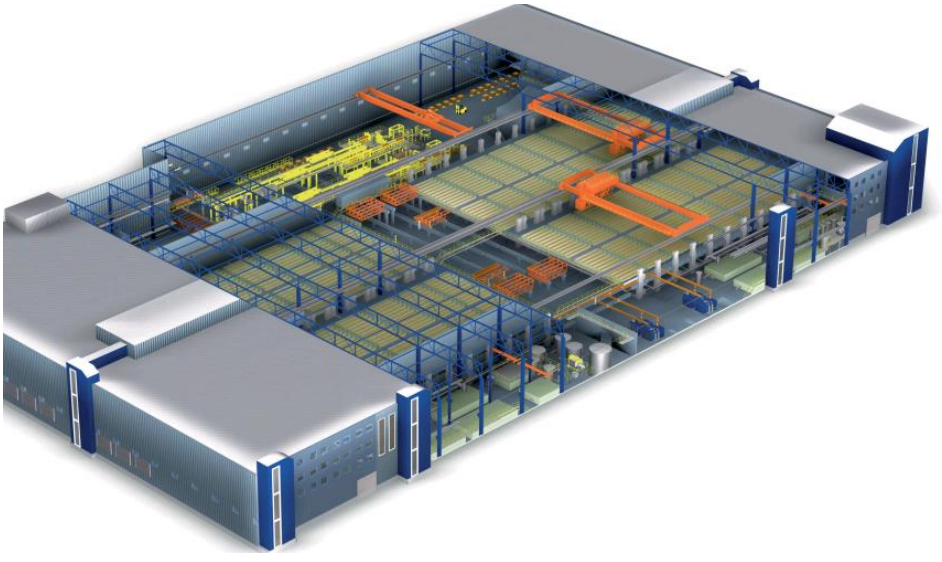


Outotec flash smelting furnace (available at http://edit.outotec.com/38424.epibrw , visited 28.11.2012)

11.7 Appendix H, Electrorefining



Electrorefining process, G. Davenport, 2011, Fig 14.1, p. 253



Outotec Oyj electrorefinery (available at http://www.outotec.com/36288.epibrw, visited 28.11.2012)

11.8 Appendix I, Literature Results From Entropy Analysis

Table 3 Entropy production of mining and beneficiation and all four metallurgical processes for the production of 1 metric ton of cathodes

Process	*Entropy production (MJ/K)*
Mining and beneficiation	36.9
Flash smelter	19.2
Converter	21.4
Anode furnace	8.3
Electrolysis	4.4
Sum metallurgy	53.3
Sum total	**90.2**

S. Gößling-Reisemann (2008), Table 3, page 574

11.9 Appendix J, Leaching Reactions

The most important copper mineral reactions which occur at $pH < 5$ are presented below for copper oxides such as Cuprite (Cu_2O), Tenorite (CuO), Azurite ($2Cu_2CO_3 \cdot Cu(OH)_2$), Malachite ($Cu_2CO_3 \cdot Cu(OH)_2$) and Chrysocolla($CuO \cdot SiO_2$) accordingly:

$$Cu_2O + 2H^+(aq) \rightarrow 2Cu^{2+} + H_2O \quad (48)$$

$$Cu_2O + H_2SO_4 \rightarrow Cu^{2+} + SO_4^{2-} + H_2O \quad (49)$$

$$2CuCO_3 \cdot Cu(OH)_2 + 3H_2SO_4 \rightarrow 3Cu^{2+} + 3SO_4^{2-} + CO_2 + 4H_2O \quad (50)$$

$$CuCO_3 \cdot Cu(OH)_2 + 2H_2SO_4 \rightarrow 2Cu^{2+} + 2SO_4^{2-} + CO_2 + 3H_2O \quad (51)$$

$$CuO \cdot SiO_2 + H_2SO_4 \rightarrow Cu^{2+} + SO_4^{2-} + SiO_2 \cdot nH_2O + (3-n)H_2O \quad (52)$$

The overall reactions for copper sulphides such as Chalcosite (Cu_2S), Covellite (CuS) and Chalcopyrite ($CuFeS_2$) are:

$$Cu_2S + 0.5O_2 + H_2SO_4 \xrightarrow[Fe^{3+},\ pH \sim 1.5\text{–}2,\ bacteria]{} Cu^{2+} + SO_4^{2-} + CuS + H_2O \quad (53)$$

$$CuS + 0.5O_2 + H_2SO_4 \xrightarrow[Fe^{3+},\ pH \sim 1.5\text{–}2,\ bacteria]{} Cu^{2+} + SO_4^{2-} + S + H_2O \quad (54)$$

$$4CuFeS_2 + 17O_2 + 4H_2SO_4 \xrightarrow[Fe^{3+},\ pH \sim 1.5\text{–}2,\ bacteria]{} 4Cu^{2+} + 4SO_4^{2-} + 2Fe_2O_3 + H_2SO_4 \quad (55)$$

The native copper can be leached similarly according to reactions:

$$Cu + 0.5O_2 + H_2SO_4 \rightarrow Cu^{2+} + SO_4^{2-} + H_2O \quad (56)$$

$$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} \quad (57)$$

11.10 Appendix K, Chemical Exergy Tables for Elements

J. Szargut, 2005, Appendix Table 3

Chemical exergies of the elements for solid reference substances										
Chemical element			Reference Species						Ch. El. Exergy	
Element	Ch.S.	noi(mol/g)	Formula	State	ci	z0	Ch. Ex.	ΔGf (kJ/mol)	Phase	**Exergy (kJ/mol)**
Aluminium	Al	2.98E-01	Al_2SiO_5	s	0.01	2.14E-01	3.83	-2440.99	s	**790.39**
Antimonium	Sb	1.64E-09	Sb_2O_5	s	0.001	1.18E-10	56.68	-829.3	s	**438.02**
Barium	Ba		$BaSO_4$	s		5.88E-06	29.85	-1361.9	s	**776.76**
Beryllium	Be	3.33E-07	Be_2SiO_4	s	0.01	2.39E-07	37.8	-2033.3	s	**604.53**
Calcium	Ca		$CaCO_3$	s		5.48E-04	18.61	-1129	s	**731.4**
Cerium	Ce	4.57E-07	CeO_2	s	0.02	1.31E-06	33.58	-1024.8	s	**1054.4**
Chromium	Cr	1.60E-06	$K_2Cr_2O_7$	s	0.01	1.15E-06	33.91	-1882.3	s	**584.49**
Cobalt	Co	2.89E-07	$CoFe_2O_4$	s	0.005	2.07E-07	38.15	-1032.6	s	**308.82**
Dysprosium	Dy	2.15E-08	$Dy(OH)_3$	s	0.02	6.17E-08	41.15	-1294.3	s	**975.35**
Erbium	Er	1.38E-08	$Er(OH)_3$	s	0.02	3.96E-08	42.25	-1291	s	**973.15**
Europium	Eu	5.79E-09	$Eu(OH)_3$	s	0.02	1.66E-08	44.41	-1320.1	s	**1004.4**
Fluorine	F2	3.30E-05	$CaF_2*3Ca_3*(PO)_2$	s	0.01	2.37E-05	26.4	-12985.3	F2.g	**481.54**
Gadolinium	Gd	1.93E-08	$Gd(OH)_3$	s	0.02	5.54E-08	41.42	-1288.9	s	**970.22**
Gallium	Ga	2.44E-07	Ga_2O_3	s	0.02	3.50E-07	36.85	-998.6	s	**514.75**
Germanium	Ge	2.20E-08	GeO_2	s	0.05	1.58E-07	38.83	-521.5	s	**556.35**
Gold	Au		Au	s		3.23E-11	59.88	0	s	**59.88**
Hafnium	Hf	3.25E-08	HfO_2	s	0.05	2.33E-07	37.86	-1027.4	s	**1061.28**
Holmium	Ho	4.85E-09	$Ho(OH)_3$	s	0.02	1.39E-08	44.85	-1294.8	s	**979.54**
Indium	In	4.36E-10	In_2O_3	s	0.05	1.56E-09	50.26	-830.9	s	**437.6**
Iridium	Ir	1.04E-13	IrO_2	s	0.005	7.46E-14	74.93	-185.6	s	**256.56**
Iron	Fe		Fe_2O_3	s		7.78E-04	17.75	-742.2	s	**376.99**
Lanthanum	La	2.16E-07	$La(OH)_3$	s	0.02	6.19E-07	35.43	-1319.2	s	**994.53**
Lutetium	Lu	1.83E-09	$Lu(OH)_3$	s	0.02	5.25E-09	47.26	-1259.6	s	**946.76**
Magnesium	Mg		$Mg_3Si_4\ O_{10}(OH)_2$	s		1.75E-04	21.45	-5543	s	**629.37**

J. Szargut, 2005, Appendix Table 4

Chemical exergies of the elements for aqueous reference substances									
Chemical Element		Reference Species						Chemical El. Exergy	
Element	Ch.S.	Formula	State	z	γ	m_n mol/kg	ΔG_f (kJ/mol)	State	Exergy kJ/mol
Arsenic	As	$HAsO_4^{-2}$	liq	-2	0.138	2.10E-08	-714.7	s	**493.83**
Bismuth	Bi	BiO^+	liq	1	0.52	1.00E-10	-146.4	s	**274.92**
Boron	B	$B(OH)_3$	liq	0	1	3.40E-04	-968.8	s	**628.6**
Bromine	Br	Br^-	liq	-1	0.73	8.70E-04	-104	Br2.l	**100.89**
Cesium	Cs	Cs^+	liq	1	0.6	2.30E-09	-282.2	s	**404.58**
Chlorine	Cl	Cl^-	liq	-1	0.63	5.66E-01	-131.26	Cl2.g	**124.03**
Cadmium	Cd	$CdCl_2$	liq	0	1	6.90E-11	-359.4	s	**293.37**
Copper	Cu	$Cu2^+$	liq	2	0.2	7.30E-10	65.5	s	**134.25**
Iodine	I	IO_3^-	liq	-1	0.6	5.20E-07	-128	I2.s	**174.74**
Lead	Pb	$PbCl_2$	liq	0	1	4.20E-11	-297.2	s	**232.4**
Lithium	Li	Li^+	liq	1	0.68	2.50E-05	-294	s	**393.03**
Mercury	Hg	$HgCl_4^{-2}$	liq	-2	0.1	3.40E-10	-446.9	l	**114.99**
Molybdenium	Mo	MoO_4^{-2}	liq	-2	0.1	1.10E-07	-836.4	s	**730.27**
Nickel	Ni	Ni^{+2}	liq	2	0.2	1.20E-07	-45.6	s	**232.7**
Phosphorous	P	HPO_4^{-2}	liq	-2	0.1	4.90E-07	-1089.3	s	**861.42**
Potasium	K	K^+	liq	1	0.62	1.06E-02	-282.4	s	**366.66**
Rubidium	Rb	Rb^+	liq	1	0.6	1.40E-06	-282.4	s	**388.89**
Selenium	Se	SeO_4^{-2}	liq	-2	0.1	1.20E-09	-441.4	s	**346.47**
Silver	Ag	$AgCl_2^-$	liq	-1	0.6	2.70E-09	-215.5	s	**69.85**
Sodium	Na	Na^+	liq	1	0.65	4.86E-01	-262.05	s	**336.71**
Sulphur	S	SO_4^{-2}	liq	-2	0.11	2.93E-02	-744.6	s	**607.05**
Wolfram	W	WO_4^{-2}	liq	-2	0.1	5.60E-10	-920.5	s	**827.46**
Zinc	Zn	Zn^{2+}	liq	2	0.2	1.70E-08	-147.3	s	**339.25**

J. Szargut, 2005, Appendix Table 2

Chemical exergies of elements for gaseous reference substances								
Chemical element		Reference Species					Ch. El. Exergy	
Element	Ch. S.	Formula	State	p 0 kPa	Ch. Ex. (kJ/mol)	ΔG_f (kJ/mol)	State	Exergy (kJ/mol)
Argon	Ar	Ar	g	9.06E-03	11.69	0	g	**11.69**
Carbon	C	CO_2	g	3.35E-04	19.87	-394.36	s..graf.	**410.25**
Helium	He	He	g	4.85E-06	30.37	0	g	**30.37**
Hydrogen	H	H_20	g	2.20E-02	9.49	-228.59	H2.g	**236.1**
Kripton	Kr	Kr	g	9.70E-07	34.36	0	g	**34.36**
Neon	Ne	Ne	g	1.77E-05	27.16	0	g	**27.16**
Nitrogen	N	N_2	g	7.58E-01	0.72	0	N2.g	**0.72**
Oxygen	O	O_2	g	2.04E-01	3.97	0	O2.g	**3.97**
Xenon	Xe	Xe	g	8.70E-08	40.33	0	g	**40.33**

Elemental exergy Table (R. Rivero and M. Garfias, 2006)

Exergy Table						
Element	phase	Ref. Substance		x,m	dG_f [kJ/mol]	**Ex el [kJ/mol]**
Ag	(s)	AgCl(s)	x	1.00E-09	-109.8	**99.3**
Al	(s)	Al_2SiO_5(s)	x	2.07E-03	-2440.99	**795.7**
Ar	(g)	Ar(g)	x	9.13E-03	0	**11.64**
As	(s)	$HAsO_4$ (-2,aq)	m	3.87E-08	-714.7	**492.6**
Au	(s)	Au(s)	x	1.36E-09	0	**50.6**
B	(s)	$B(OH)_3$(aq)	m	3.42E-04	-968.84	**628.1**
Ba	(s)	$BaSO_4$(s)	x	4.20E-06	-1361.9	**775.4**
Be	(s)	Be_2SiO_4(s)	x	2.10E-07	-2033.3	**604.3**
Bi	(s)	BiO(+1,aq)	m	9.92E-11	-146.4	**274.8**
Br2	(l)	Br(-1,aq)	m	8.73E-04	-103.97	**101**
C	(s)	CO_2(g)	x	3.37E-04	-394.38	**410.27**
Ca	(s)	$CaCO_3$(s)	x	1.40E-03	-1129	**729.1**
Cd	(s)	$CdCO_3$(s)	x	1.22E-08	-669.4	**298.4**
Ce	(s)	CeO_2(s)	x	1.17E-06	-1024.8	**1054.7**
Cl2(g)	(g)	Cl(-1,aq)	m	0.5658	-131.26	**123.7**
Co	(s)	$CoFe_2O_4$(s)	x	2.85E-07	-1032.6	**313.4**
Cr	(s)	$K_2Cr_2O_7$(s)	x	1.35E-06	-1882.3	**584.4**
Cs	(s)	Cs(+1,aq)	m	2.34E-09	-282.23	**404.6**
Cu	(s)	$CuCO_3$(s)	x	5.89E-06	-518.9	**132.6**
D2	(g)	D_2O(g)	x	3.37E-06	-234.63	**263.9**
Dy	(s)	$Dy(OH)_3$(s)	x	4.88E-08	-1294.3	**976**
Er	(s)	$Er(OH)_3$(s)	x	4.61E-08	-1291	**972.8**
Eu	(s)	$Eu(OH)_3$(s)	x	2.14E-08	-1320.1	**1003.8**
F2	(g)	CaF_2*$3Ca_3(PO_4)_2$(s)	x	2.24E-04	-12985.3	**505.8**
Fe	(s)	Fe_2O_3(s)	x	6.78E-03	-742.2	**374.3**
Ga	(s)	Ga_2O_3(s)	x	2.98E-07	-998.6	**515**
Gd	(s)	$Gd(OH)_3$(s)	x	9.21E-08	-1288.9	**969**
Ge	(s)	GeO_2(s)	x	9.49E-08	-521.5	**557.7**
H2	(g)	H_2O(g)	x	2.17E-02	-228.59	**236.12**
He	(g)	He(g)	x	4.89E-06	0	**30.31**
Hf	(s)	HfO_2(s)	x	1.15E-07	-1027.4	**1063.1**
Hg	(l)	$HgCl_2$(s)	x	5.42E-10	-178.7	**107.9**
Ho	(s)	$Ho(OH)_3$(s)	x	1.95E-08	-1294.8	**978.7**
I2	(s)	IO_3 (-1,aq)	m	5.23E-07	-128	**175.7**
In	(s)	In_2O_3(s)	x	2.95E-09	-830.9	**436.9**
Ir	(s)	IrO_2(s)	x	3.59E-12	-185.6	**247**
K	(s)	K(+1,aq)	m	1.04E-02	-282.44	**366.7**
Kr	(g)	Kr(g)	x	9.78E-07	0	**34.3**

Element	phase	Ref. Substance		x,m	dG_f [kJ/mol]	**Ex el [kJ/mol]**
La	(s)	$La(OH)_3(s)$	x	5.96E-07	-1319.2	**994.7**
Li	(s)	Li(+1,aq)	m	2.54E-05	-294	**392.7**
Lu	(s)	$Lu(OH)_3(s)$	x	7.86E-09	-1259.6	**945.8**
Mg	(s)	$Mg_3Si_4O_{10}(OH)_2(s)$	x	8.67E-04	-5543	**626.9**
Mn	(s)	$MnO_2(s)$	x	2.30E-05	-465.2	**487.7**
Mo	(s)	$MoO_4(-2,aq)$	m	1.08E-07	-836.4	**731.3**
N2	(g)	$N_2(g)$	x	0.7634	0	**0.67**
Na	(s)	Na(+1,aq)	m	0.4739	-262.0	**336.7**
Nb	(s)	$Nb_2O_3(s)$	x	1.49E-07	-1766.4	**899.7**
Nd	(s)	$Nd(OH)_3(s)$	x	5.15E-07	-1294.3	**970.1**
Ne	(g)	Ne(g)	x	1.76E-05	0	**27.14**
Ni	(s)	NiO(s)	x	1.76E-06	-211.7	**242.6**
O2	(g)	$O_2(g)$	x	0.2054	0	**3.92**
Os	(s)	$OsO_4(s)$	x	3.39E-13	-305.1	**368.4**
P	(s)	$HPO_4(-2,aq)$	m	4.86E-07	-1089.3	**861.3**
Pb	(s)	$PbCO_3(s)$	x	1.04E-07	-625.5	**249.2**
Pd	(s)	PdO(s)	x	6.37E-11	-82.5	**138.7**
Pr	(s)	$Pr(OH)_3(s)$	x	1.57E-07	-1285.1	**963.9**
Pt	(s)	$PtO_2(s)$	x	1.76E-11	-83.7	**141.2**
Pu	(s)	$PuO_2(s)$	x	8.40E-20	-995.1	**1100.1**
Ra	(s)	$RaSO_4(s)$	x	2.98E-14	-1364.2	**824.2**
Rb	(s)	Rb(+1,aq)	m	1.46E-06	-282.4	**388.7**
Re	(s)	$Re_2O_7(s)$	x	3.66E-12	-1067.6	**559.6**
Rh	(s)	$Rh_2O_3(s)$	x	3.29E-12	-299.8	**179.7**
Ru	(s)	RuO2(s)	x	6.78E-13	-253.1	**318.6**
S	(s)	$SO_4(-2,aq)$	m	1.24E-02	-744.63	**609.3**
Sb	(s)	$Sb_2O_5(s)$	x	1.08E-10	-829.3	**438.2**
Sc	(s)	$Sc_2O_3(s)$	x	3.73E-07	-1819.7	**925.3**
Se	(s)	$SeO_4(-2,aq)$	m	1.18E-09	-441.4	**347.5**
Si	(s)	$SiO_2(s)$	x	0.407	-856.7	**855**
Sm	(s)	$Sm(OH)_3(s)$	x	1.08E-07	-1314	**993.7**
Sn	(s)	$SnO_2(s)$	x	4.61E-07	-519.6	**551.8**
Sr	(s)	$SrCO_3(s)$	x	2.91E-05	-1140.1	**749.8**
Ta	(s)	$Ta_2O_5(s)$	x	7.45E-09	-1911.6	**974.1**
Tb	(s)	$Tb(OH)_3(s)$	x	1.71E-08	-1314.2	**998.5**
Te	(s)	$TeO_2(s)$	x	9.48E-12	-270.3	**329.3**
Th	(s)	$ThO_2(s)$	x	2.71E-07	-1169.1	**1202.7**
Ti	(s)	$TiO_2(s)$	x	1.63E-04	-889.5	**907.2**
Tl	(s)	$Tl_2O_4(s)$	x	1.49E-09	-347.3	**194.9**
Tm	(s)	$Tm(OH)_3(s)$	x	7.59E-09	-1265.5	**951.8**
U	(s)	$UO_3*H_2O(s)$	x	1.49E-08	-1395.9	**1196.6**

Element	phase	Ref. Substance		x,m	dG_f [kJ/mol]	**Ex el [kJ/mol]**
V	(s)	VO_5(s)	x	1.83E-06	-1419.6	**721.3**
W	(s)	WO_4(-2,aq)	m	5.64E-10	-920.5	**828.5**
Xe	(g)	Xe(g)	x	8.81E-08	0	**40.27**
Y	(s)	$Y(OH)_3$	x	1.00E-06	-1291.4	**965.6**
Yb	(s)	$Yb(OH)_3$(s)	x	4.61E-08	-1262.5	**944.3**
Zn	(s)	$ZnCO_3$(s)	x	7.45E-06	-731.6	**344.7**
Zr	(s)	$ZrSiO_4$(s)	x	2.44E-05	-1919.5	**1083**
State: solid (s), gaseous (g), liquid (l) and aqueous (aq.)						

11.11 Appendix L, Calculation Examples for Exergy

In this section it is demonstrated how exergy of flow is calculated in some cases. These cases are: one component flow, liquid phase of metals (same calculations apply for solids, thus only one example of this is shown), and aqueous mixture of water soluble components.

11.11.1 Exergy of One Component Flow

This is the simple case where we have only one component present in the flow. As an example, exergy calculations for gaseous flow of water to dryer from PS-process model SD 1 unit are presented.

The initial data are:

n=22.57 mol,

$T = 198.00$ °C, p = 14.98 bar, H_2O(g),

$T_0 = 298.15K$, $p_0 = 1bar$, H_2O(l)

The values required for calculation of exergy for 1 kmol, enthalpy H, entropy S, and Gibbs free energy G, can be obtained from HSC database (from water mode):

H(T,p,g) = -237.475 kJ/mol

S(T,p,g) = 0.180 J/molK

H(T_0, p_0, l) = -285.827 kJ/mol

S(T_0, p_0, l) = 0.070 J/molK

$\Delta G_f^0 (T_0, p_0, l)$ = -306.685 kJ/mol

The physical exergy of the system can be solved using equation 2 from Chapter 3.3.1:

$$B_{PH} = \mathrm{H(T,p,g)} - \mathrm{H}(T_0, p_0, l) - T_0\,[\mathrm{S(T,p,g)} - \mathrm{S}(T_0, p_0, l)\,]$$

$$B_{PH} = -237.475\frac{J}{mol} - \left(-285.827\frac{\mathrm{kJ}}{\mathrm{mol}}\right) - 298.15\mathrm{K}\left(0.180\frac{\mathrm{J}}{\mathrm{molK}} - 0.070\frac{\mathrm{J}}{\mathrm{molK}}\right) = 63.86\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Besides this the chemical exergy needs to be solved. The Gibbs free energy was from the HSC database but besides this the latter term in the equation 6 from Chapter 3.3.1, that is the elemental exergy, needs to be solved:

$$B_{CH,el} = \sum_{el,i} n_{el,i} B^0_{CH,el,i}$$

From the Table in appendix K we can get the elemental exergy values for H2 and O_2 that are required to calculate the elemental exergy.

$$n_{el,H2} B^0_{CH,el,H2} = 1 \times 236.12 \frac{kJ}{mol} = 236.12 \frac{kJ}{mol}$$

$$n_{el,O2} B^0_{CH,el,O2} = 0.5 \times 3.92 \frac{\text{kJ}}{\text{mol}} = 1.96 \frac{kJ}{mol}$$

$$\sum_{el,i} n_{el,i} B^0_{CH,el,i} = 236.12 \frac{kJ}{mol} + 1.96 \frac{kJ}{mol} = 238.08 \frac{kJ}{mol}$$

Now the chemical exergy is:

$$B^0_{CH} = \Delta_f G^0_{H_2O}(T_0, p_0, l) + \sum_{el,i} n_{el,i} B^0_{CH,el,i} = -306.685 \frac{\text{kJ}}{\text{mol}} + 238.08 \frac{\text{kJ}}{\text{mol}} = -68.61 \frac{kJ}{mol}$$

Combining the chemical and physical exergies gives:

$$B = [B^0_{CH} + B_{PH}] = \left[-68.61 \frac{kJ}{mol} + 63.86 \frac{\text{kJ}}{\text{mol}}\right] = 0.25 \frac{kJ}{mol}$$

$$B_{tot} = nB = 0.25 \frac{kJ}{mol} \times 22.57\ mol = 5.42\ kJ$$

11.11.2 Exergy of Mixing

The exergy of mixing of metals in this model is following the ideal gas assumption for other than aqueous solutions (which will be discussed in the next Chapter). Mixing causes losses of exergy that needs to be taken into account in both chemical and physical exergy through mixing entropy (physical) and mixing free energy (chemical). This gives us equation 10 from Chapter 3.3.1 that can be used for calculating chemical exergy for such case:

$$B_{CH} = \sum_i \ n_i x_i \left(\Delta_f \boldsymbol{G_i^0} + \sum_{el,i} n_{el,i} B^0_{CH,el,i}\right) + RT \ \ \sum_i \ n_i x_i ln \boldsymbol{x_i}$$

The entropy of mixing should be calculated at the specific temperature and this entropy should be added to the physical exergy:

$$S_{mix} = -RT \sum_i \ x_i ln(x_i)$$

$$B_{PH} = \sum_{\mathrm{i}} \{\mathrm{H_i(T,p,g)} - \mathrm{H_i}(T_0, p_0, l) - T_0 \ [\mathrm{S_i(T,p,g)} - \mathrm{S_i}(T_0, p_0, l) \ ]\} - RT \sum_i \ x_i ln(x_i)$$

Now as an example a stream is chosen to demonstrate the application of these equations. The contents of the example stream are shown in the Table below.

Table 34, Contents of the example stream

SULPHIDE STREAM	Content	Amount
T	mol-%	mol
1473.15 K	100.00	500.00
Cu_2S	68.00	340.00
FeS	5.00	25.00
Fe_3O_4	5.00	25.00
Ni_3S_2	20.00	100.00
As_2S_3	0.10	0.50
PbS	1.90	9.50

The calculations are demonstrated for one substance, the Cu2S in this case, while the rest of the results are shown in the Table 33. The following values for Cu_2S were retrieved from the HSC.

H(T,p,s) = 34.71 kJ/mol

S(T,p,s) = 0.277 J/molK

H(T_0, p_0, s) = -83.36 kJ/mol

S(T_0, p_0, s) = 0.116 J/molK

$\Delta G_f^0 (T_0, p_0, s)$ = -118.03 kJ/mol

$$B^0_{CH,el} = \sum_{el,i} n_{el,i} B^0_{CH,el,i} = \mathbf{2 \times 132.6 \frac{kJ}{mol} + 1 \times 609.3 \frac{kJ}{mol} = 874.5 \frac{kJ}{mol}}$$

Besides these we need to add the Gibbs free energy of mixing and entropy of mixing to the equations. The calculations are based on ideal gas assumption and the molar quantity is only taken into account in the end. The Gibbs free energy of mixing is given by:

$$\Delta G_{mix} = RT \sum_i \ x_i ln x_i$$

And the entropy of mixing is given by:

$$S_{mix} = -R\sum_i \ x_i ln x_i$$

Or if we want to express this in more conveniently [using J/mol]:

$$S_{mix} = -RT\sum_i \ x_i ln x_i$$

T refers to the temperature of the mixture. It is convenient to calculate the share of single components:

$$\Delta G_{mix,i} = RT_0 x_i ln x_i = 8.314\frac{\boldsymbol{J}}{\boldsymbol{molK}} \times 298.15K \times 0.68 \times ln0.68 = -0.65\frac{kJ}{mol}$$

And similarly for the entropy:

$$S_{mix,i} = -RT_0 x_i ln x_i = 8.314\frac{J}{molK} \times 298.15K \times 0.68 \times ln0.68 = 0.65kJ/mol$$

Now we can express the physical exergy as:

$$B_{Ph} = H - H_0 - T(S - S_0) - RT\sum_i \ x_i ln x_i$$

Or for a single component in this example:

$$B_{PH} = \mathrm{H_i(T, p, g)} - \mathrm{H_i}(T_0, p_0, l) - T_0\ [\mathrm{S_i(T, p, g)} - \mathrm{S_i}(T_0, p_0, l)\ ] - RTx_i ln x_i$$

$$B_{PH} = 34.71\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} - \left(-83.36\frac{\boldsymbol{kJ}}{\boldsymbol{mol}}\right) - 298.15K \times \left[\left(0.277\frac{\boldsymbol{J}}{\boldsymbol{Kmol}}\right) - \left(0.116\frac{\mathrm{J}}{\mathrm{molK}}\right)\right] + 0.65\frac{kJ}{mol} = 70.84\frac{kJ}{mol}$$

Similarly the chemical exergy for a single component becomes:

$$B_{CH} = \Delta_f G_i^0 + \sum_{el,i} n_{el,i} B_{CH,el,i}^0 + RT\ \ x_i ln x_i = -118.03\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} + 874.5\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} + \left(-0.65\frac{\boldsymbol{kJ}}{\boldsymbol{mol}}\right) = 755.82\frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

$$B = B_{PH} + B_{CH} = 70.84\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} + 755.82\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} = 826.66\frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

And finally the total chemical exergy gives:

$$B_{tot} = nB = 340.00mol \times 826.66\frac{\boldsymbol{kJ}}{\boldsymbol{mol}} = 281064\ kJ$$

Table 35, Values for the example stream

Substance	B Ch (kJ/mol)	B Ph (kJ/mol)	B (kJ/mol)	B tot (kJ/mol)
Cu_2S	753.3	73.4	826.7	281062
FeS	863.7	73.2	936.9	23423
Fe_3O_4	-30.9	148.1	117.2	2929
Ni_3S_2	1686.2	176.3	1862.4	186242
As_2S_3	2671.5	138.3	2809.8	1405
PbS	729.9	79.1	809.0	7685
Total	6673.6	688.3	7361.9	502746

The calculations on excel for B Ch and B Ph are demonstrated in the Table 34 below by connecting the components of exergy calculation together.

Table 36, Example of exergy calculation on excel

Example stream							
	T	1473.15	K				
	T ref	298.15	K				
Substance	**ΔfG0 [kJ/mol]**	**Amount [mol]**	**Mole fraction**	**H [J/mol]**	**H0 [kJ/mol]**	**S [J/mol]**	**S0 [J/molK]**
Cu_2S	-101.49	340.00	0.68	12.22	-71.67	238.09	100.00
FeS	-101.51	25.00	0.05	12.05	-86.04	165.02	51.90
Fe_3O_4	-997.29	25.00	0.05	-193.46	-859.80	402.84	125.75
Ni_3S_2	-220.37	100.00	0.20	-235.97	-186.12	401.51	114.87
As_2S_3	-121.68	0.50	0.00	-82.62	-79.76	469.45	140.59
PbS	-109.80	9.50	0.02	-320.14	-86.40	133.29	78.47

$$B_{CH} = \sum_i n_i x_i \left[\Delta_f G_i^0 + \sum_{el,i} n_{el,i} B_{CH,el,i}^0 \right] + RT_0 \sum_i n_i x_i \ln x_i \qquad B_{PH} = \sum_i \left[H_i - H_{0,i} - T_0 (S_i - S_{0,i}) \right] - RT \sum_i x_i \ln x_i$$

Substance	**ΔGmix [kJ/mol]**	**B el [kJ/mol]**	**B Ch [kJ/mol]**	**S mix [kJ/mol]**	**B Ph,i kJ/mol**	**B Ph [kJ/mol]**	**B tot [kJ/mol]**
Cu_2S	-0.56	751.93	**649.89**	0.56	4.95	**1.53**	**651.42**
FeS	-0.32	845.74	**743.91**	0.32	5.25	**1.55**	**745.46**
Fe_3O_4	-0.32	972.26	**-25.35**	0.32	13.33	**3.79**	**-21.56**
Ni_3S_2	-0.69	1673.60	**1452.55**	0.69	8.07	**2.43**	**1454.98**
As_2S_3	-0.01	2418.83	**2297.14**	0.01	5.07	**1.41**	**2298.55**
PbS	-0.16	738.18	**628.22**	0.16	7.68	**2.18**	**630.40**

11.11.3 Exergy of Mixing in Non-Ideal Solution

The mixing of non-ideal solutions is slightly more complicated as the activities should be used instead of mole fractions. The calculation of activities which is available in HSC is based on Pitzer-equations which will not be discussed here in detail as this goes beyond the scope of this Thesis. Stream that will be discussed here is introduced in the Table 9. The calculation example here is based on the values of OH(-a) (or commonly oH^--ion) as the values for the whole stream can be found in the Table 35. It should be noted that the sum of electrons do not balance here as this is only a demonstration of the calculation methods.

Table 37, Example aqueous stream

WATER STREAM	Content	Amount
T	mol-%	mol
323.15 K	100.00	500.00
H_2O	68.00	340.00
H(+a)	6.00	30.00
OH(-a)	6.00	30.00
Cu(+2a)	5.00	25.00
Fe(+2a)	5.00	25.00
SO_4(-2a)	10.00	50.00

Now taking the activity coefficients into account will change the equation for chemical exergy into the form:

$$B_{CH,mix} = \sum_i n_i x_i B^0_{CH,i} + RT_0 \sum_i n_i x_i ln\gamma_i x_i$$

$$a_i = \gamma_i x_i$$

Using HSC it was possible to get values for the following thermodynamic terms:

H(T,p,s) = -55.68 kJ/mol

S(T,p,s) = -4.84 J/molK

H(T_0, p_0, s) = -54.98 J/mol

S(T_0, p_0, s) = -2.56 J/molK

$\Delta G_f^0 (T_0, p_0, s)$ = -54.21 kJ/mol

γ = 0.21 (obtainable from HSC aqua mode)

$$B^0_{CH,el,i} = \sum_{el,j} n_{el,j} B^0_{CH,el,j} = 0.5 \times 236.12 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} + 0.5 \times 3.92 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} = 120.02 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

The Gibbs free energy of mixing as well as entropy of mixing allocated by the substance in question needs to be calculated as previously, but now we need the activity coefficient:

$$\Delta G_{mix,i} = RT_0 x_i ln x_i \gamma_i = 8.314 \frac{\boldsymbol{J}}{\boldsymbol{molK}} \times 298.15\ K \times 0.06 \ln(0.06 \times 0.21) = -0.65 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

$$S_{mix,i} = -RT_0 x_i ln \gamma x_i = 8.314 \frac{\boldsymbol{J}}{\boldsymbol{molK}} \times 298.15\ K \times 0.06 \ln(0.21 \times 0.06) = 0.65 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

Using elemental exergy and gibbs free energy of mixing the chemical exergy becomes:

$$B_{CH,mix,i} = 120.02 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} - 0.65 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} = 119.37 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

While the physical exergy can be calculated using:

$$B_{PH} = \mathrm{H_i(T, p, g)} - \mathrm{H_i}(T_0, p_0, l) - T_0\ [\mathrm{S_i(T, p, g)} - \mathrm{S_i}(T_0, p_0, l)\ ] - RTx_i ln\gamma_i x_i$$

$$B_{PH} = -55.68 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} - \left(-54.98 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}}\right) - 298.15\mathrm{K}\left[-4.84 \frac{\boldsymbol{J}}{\boldsymbol{molK}} - (-2.56 \frac{\boldsymbol{J}}{\boldsymbol{molK}})\right] + 0.65 \frac{\mathrm{kJ}}{\mathrm{kmol}} = 0.63 \frac{kJ}{mol}$$

Finally the Chemical exergy of the substance can be calculated:

$$B_i = B_{Ch,i} + B_{Ph,i} = 119.37 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} + 0.63 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} = 120.02 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}}$$

And for the whole stream we have:

$$B_{i,tot} = nB_i = 30\ mol * 120.02 \frac{\boldsymbol{kJ}}{\boldsymbol{mol}} = 3600.6\ kJ$$

The rest of the results are in the Table 36 as noted before:

Table 38, Exergy of example flow

Substance	Ex Ch (kJ/mol)	Ex Ph (kJ/mol)	Ex (kJ/mol)	Ex tot (kJ/mol)
H_2O	-16.47	0.05	**-16.42**	**-5581.88**
H(+a)	56.08	0.31	**56.40**	**1691.89**
OH(-a)	2.50	0.13	**2.62**	**78.71**
Cu(+2a)	53.87	0.29	**54.17**	**1354.13**
Fe(+2a)	74.65	0.24	**74.89**	**1872.18**
SO_4(-2a)	-71.02	-0.37	**-71.39**	**-3569.72**
Total	99.61	0.65	**100.26**	**-4154.68**

11.12 Appendix M, List of Process Units

Process	Flotation
Unit name	**Type**
Grinding	Grinder
Conditioner	Conditioner
Rougher flotation	Flotation
Rougher Scavenger	Scavenger
Tail Sump	Sump
TailsThickener	Thickener
ConcentrateThickener	Thickener
PFSump	Sump
ConCFilter	Filter
Pond	Pond
WaterTank	Tank
RghScavConcSump	Sump
Clnr1F	Feed
Cleaner1	Cleaner
Clnr2F	Feed
Cleaner2	Cleaner
Clnr3F	Feed
Cleaner3	Cleaner
ConcSump	Sump

Process	Electrorefining
Unit name	**Type**
CuER	Electrorefining
Crystallization	Crystallization
Cu EW	Electrowinning
Cu_3As EW	Electrowinning
Evaporation	Evaporation
SeAg Prec	Precipitation
Se Roasting	Furnace
Dore	Casting
Leaching	Leaching
Te Cementation	Cementation
H_2SO_4 division	Separator
Washing	Washer
Precious metals handling	Electrorefining

Process	FSF-PS
Unit name	**type**
SD1	Steam dryer
SD2	Steam dryer
SD mixer 1	Mixer
SD mixer 2	Mixer
FSF	Flash Smelting Furnace
FSF UP	Gas uptake
WHBFSF	Waste heat boiler
ESPFSF	Electrostatic Precipitator
PS_sb	Peirce-Smith Converter
PS_cb	Peirce-Smith Converter
PS_sr	Peirce-Smith Converter
PS_s2af	Peirce-Smith Converter
WHB_PS	Waste heat boiler
ESP_PS	Electrostatic Precipitator
AFOX	Anode Furnace
AFRE	Anode Furnace
anode handling	Casting
SC	Scavenger

Process	FSF-FCF
Unit name	**type**
SD1	Steam dryer
SD2	Steam dryer
SD mixer 1	Mixer
SD mixer 2	Mixer
FSF	Flash Smelting Furnace
FSFUP	Uptake of furnace gases
FSF Matte granulation	Granulation
WHBFSF	Waste heat boiler
ESPFSF	Electrostatic precipitator
FCF	Flash Converting Furnace
FCF_UP	Uptake of furnace gases
FCF slag granulation	Granulation
WHB_FCF	Waste heat boiler
ESP_FCF	Electrostatic precipitator
AFOX	Anode furnace
AFRE	Anode furnace
Anode handling	Casting
SC	Scavenger

11.13 Appendix N, Exergies of Concentration Streams

FSF-PS	Ex Ch	Ex Ch	Ex Total
Concentration	GJ	water GJ	GJ
BALANCE TOTAL:	**0.45**	**0.11**	**0.56**
FreshWater	0.00	2.52	2.52
Ore Feed	561.96	0.00	561.96
INPUT TOTAL:	**561.96**	**2.52**	**564.48**
FinalConcentrate	31.40	0.01	31.41
TailSolids	531.01	0.00	531.01
WaterOutlet	0.00	2.61	2.61
OUTPUT TOTAL:	**562.41**	**2.62**	**565.03**
Clnr1C	138.28	2.42	140.70
Clnr1F	542.41	8.61	551.01
Clnr1T	404.14	6.18	410.33
Clnr2C	63.02	1.23	64.26
Clnr2F	169.90	3.02	172.92
clnr2T	106.87	1.79	108.66
Clnr3C	31.40	0.64	32.03
Clnr3F	63.02	1.23	64.26
clnr3T	31.63	0.60	32.22
ConcFiltrate	0.31	0.10	0.42
ConcThickenerOF	0.00	0.63	0.63
ConcThickenerUF	31.71	1.13	32.84
FinalConcentrateSL	31.40	0.64	32.03
FinalTail	531.01	8.77	539.78
FlotationFeed	561.96	9.30	571.26
MillWater	0.00	9.30	9.30
PFfeed	31.71	1.13	32.84
RghConc	280.11	4.16	284.27
RghFeed	562.31	9.41	571.71
RghScanConc	435.53	6.82	442.35
RghScavTail	531.01	8.77	539.78
RghTail	686.43	11.44	697.87
ScavConc	155.42	2.67	158.09
TailsThickenerOF	0.00	6.16	6.16
TailsThickenerUF	531.01	2.61	533.62

FSF-FCF Process	Ex Ch	Ex water	Ex Total
Concentration	[GJ/t Cu]	[GJ/t Cu]	[GJ/t Cu]
BALANCE TOTAL:	**0.5**	**0.1**	**0.6**
FreshWater	0.0	2.5	**2.5**
Ore Feed	566.0	0.0	**566.0**
INPUT TOTAL:	**566.0**	**2.5**	**568.5**
FinalConcentrate	31.6	0.0	**31.6**
TailSolids	534.8	0.0	**534.8**
WaterOutlet	0.0	2.6	**2.6**
OUTPUT TOTAL:	**566.4**	**2.6**	**569.1**
Clnr1C	139.3	2.4	**141.7**
Clnr1F	546.3	8.7	**554.9**
Clnr1T	407.0	6.2	**413.3**
Clnr2C	63.5	1.2	**64.7**
Clnr2F	171.1	3.0	**174.2**
clnr2T	107.6	1.8	**109.4**
Clnr3C	31.6	0.6	**32.3**
Clnr3F	63.5	1.2	**64.7**
clnr3T	31.9	0.6	**32.5**
ConcFiltrate	0.3	0.1	**0.4**
ConcThickenerOF	0.0	0.6	**0.6**
ConcThickenerUF	31.9	1.1	**33.1**
FinalConcentrateSL	31.6	0.6	**32.3**
FinalTail	534.8	8.8	**543.6**
FlotationFeed	566.0	9.4	**575.3**
MillWater	0.0	9.4	**9.4**
PFfeed	31.9	1.1	**33.1**
RghConc	282.1	4.2	**286.3**
RghFeed	566.3	9.5	**575.8**
RghScanConc	438.6	6.9	**445.5**
RghScavTail	534.8	8.8	**543.6**
RghTail	691.3	11.5	**702.8**
ScavConc	156.5	2.7	**159.2**
TailsThickenerOF	0.0	6.2	**6.2**
TailsThickenerUF	534.8	2.6	**537.4**

11.14 Appendix O, Exergy Calculations of Fuels

Table 39, LFO exergy calculation (HSC)

LIGHT FUEL OIL				
IN	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Fuel Oil	1	0	42.58	42.58
Air	13.00	0	0.63	0.63
Total	**14.00**	**0**	**43.20**	**43.20**
OUT	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Flue gases	14.00	0	2.40	2.40
Total	**14.00**	**0**	**2.40**	**2.40**
Balance	0	0	40.80	40.80

Table 40, Coke exergy calculation (HSC)

COKE				
IN	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Coal	1.00	0	9.14	9.14
Air	9.96	0	0.13	0.13
Total	**10.96**	**0**	**9.28**	**9.28**
OUT	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Process gas	10.89	0	0.51	0.51
Ash	0.07	0	0.01	0.01
Total	**10.96**	**0**	**0.52**	**0.52**
Balance	**0**	**0**	**8.75**	**8.75**

Table 41, Propane exergy calculation (HSC)

PROPANE				
IN	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Propane	1	0	48.78	48.78
Air	14.89	0	0.72	0.72
Total	**15.89**	**0**	**49.50**	**49.50**
OUT	**Amount (kg)**	**B Ph [MJ]**	**B Ch (MJ)**	**B tot (MJ)**
Flue gases	15.89	0	2.48	2.48
Total	**15.89**	**0**	**2.48**	**2.48**
Balance	**0**	**0**	**47.01**	**47.01**

11.15 Appendix P, Inputs and Outputs of Processes

Input streams for FSF-FCF process		
Input stream	amount	
Ore	97.8	kg/kg Cu
Water	48.7	kg/kg Cu
Silica flux	0.57	kg/kg Cu
Air (2 m-% water)	3.62	kg/kg Cu
Conc. Technical Oxygen (95%)	1.40	kg/kg Cu
Lime Stone	0.13	kg/kg Cu
Fuel Oils	0.06	kg/kg Cu
Natural Gas	0.0007	kg/kg Cu
Propane	0.014	kg/kg Cu
Anode SO_4	0.0002	kg/kg Cu
Na_2CO_3	0.0005	kg/kg Cu
$Na_2B_4O_7$	0.001	kg/kg Cu
H_2SO_4	0.031	kg/kg Cu
Electricity	11.7	MJ/kg Cu
Output streams for FSF-FCF process		
Water	52.96	kg/kg Cu[51]
Ore	93.74	kg/kg Cu
Flue gas	0.47	kg/kg Cu
Heavy metal dust	0.011	kg/kg Cu
Carbon dioxide	0.16	kg/kg Cu
Acid gas (appr. 38 m-% SO_2)	4.45	kg/kg Cu
Steam dryer off-gas (46 m-% water)	1.48	kg/kg Cu
Tailings	2.78	kg/kg Cu
Heat Loss	6.62	MJ/kg Cu
Cathode Copper	1.00	kg/kg Cu
Oxygen	0.004	kg/kg Cu
Cu_3As	0.07	kg/kg Cu
$NiSO_4$, H_2O, H_2SO_4 solution	0.04	kg/kg Cu
Selenium	0.003	kg/kg Cu
Heavy metal dust	0.003	kg/kg Cu
Slag	0.01	kg/kg Cu
CO_2, H_2O	0.002	kg/kg Cu
Sulphuric Acid 98%	0.01	kg/kg Cu
CuTe	0.002	kg/kg Cu
H_2SO_4 70%	0.03	kg/kg Cu

[51] Not all sources of water are visible in the input side

Input streams for FSF-PS Process		
Ore	97.1	kg/kg Cu
Water	51.32	kg/kg Cu
Silica flux	0.61	kg/kg Cu
Air	5.30	kg/kg Cu
Conc Technical Oxygen	0.90	kg/kg Cu
Fuel Oil	0.004	kg/kg Cu
Natural gas	0.005	kg/kg Cu
Light fuel oil	0.024	kg/kg Cu
Propane	0.015	kg/kg Cu
Coke	0.014	kg/kg Cu
Anode SO_4	0.0002	kg/kg Cu
Na_2CO_3	0.0005	kg/kg Cu
$Na_2B_4O_7$	0.001	kg/kg Cu
H_2SO_4	0.031	kg/kg Cu
Electricity	11.7	MJ/kg Cu

Output Streams for FSF-PS Process		
Water	52.58	kg/kg Cu
Ore	93.07	kg/kg Cu
Flue gas	0.35	kg/kg Cu
Dust	0.011	kg/kg Cu
CO_2	0.025	kg/kg Cu
Sulphuric aerosol (25 m-% SO_2)	7.87	kg/kg Cu
Steam-dryer off-gas	1.37	kg/kg Cu
Tailings	2.74	kg/kg Cu
Heat Loss	6.57	kg/kg Cu
Cathode Copper	1.00	kg/kg Cu
Oxygen	0.004	kg/kg Cu
Cu_3As	0.07	kg/kg Cu
$NiSO_4$, H_2O, H_2SO_4 solution	0.04	kg/kg Cu
Selenium	0.003	kg/kg Cu
Heavy metal dust	0.003	kg/kg Cu
Slag	0.01	kg/kg Cu
CO_2, H_2O	0.002	kg/kg Cu
Sulphuric Acid 98%	0.01	kg/kg Cu
CuTe	0.002	kg/kg Cu
H_2SO_4 70%	0.03	kg/kg Cu

11.16 Appendix Q, HSC-Sim ™ Errors and Suggestions

An error was found when a mapped stream was removed, there remained a ghost mapping in the file where the mapping data was saved which was solved.

Another problem with mapping that was found when some stream was mapped and the mapping was removed and mapped again, then the stream showed as if it was not mapped but after normalization the mapped value occurred.

Some problems with the normalization of manual electricity input was found as well as some problems with disappearances of mappings were found which were corrected in co-operation with the programmers.

The crushing of the HSC-Sim ™ program was encountered several times and the procedures that had been taken before the crushes were described for the programmers together with a print screen of the error, which then helped the programmers to identify the problem. Found and solved "Run time errors" were as follows: Run time error '13': Type mismatch, Run time error '35603': Invalid key (in two separate occasions), Run time error '20477': Invalid file name, Run time error '20007': Invalid cell reference.

A suggestion was made for a notification in case if the CO_2 is mapped in the manual output side so that there appears a message that warns of the possibility of double accounting for the CO_2 in case if the fuels in input are mapped. This suggestion was accepted for HSC.

A suggestion for the possibility to divide the streams in the components was made for being able to do mapping for all streams. This feature was discussed but at this point it was not added.

There were also some sources of error in the models that needed to be corrected. For example in the models for FSF-PS flash smelter there were some streams that had been linked twice on one unit resulting in ghost stream, which then needed to be removed.

The list of suggestions on what needs to be done:

- Complete the model for acid plant, adjust it according to the existing model's off-gas contents and include it to the system.
- Include the fugitive emissions to the models (based on measurements).

- More precise energy consumption information needs to be acquired so that electricity consumption can be allocated exactly to the units and this data needs to be included to the models for more exact exergy efficiency calculations.
- The exergy related to the area formation needs to be experimented.
- Exergy calculation for ideal and non-ideal mixing needs to be included to the exergy calculation scheme of HSC-Sim™ to improve the calculation accuracy. The calculation scheme for non-ideal mixing should be developed according to the scheme represented below based on e-mails sent to A. Roine. The Ideal mixing calculation scheme replaces γ_i in the calculations with 1.

Including the exergy of non-ideal mixing to the calculation scheme of HSC-Sim™

Pizer model activity coefficient calculation (included with current activity coefficient calculations):

$$\ln \gamma_{+,M} = z_+^2 F + \sum_a m_a \left(2B_{Ma} + ZC_{Ma} \right) + 2 \sum_n m_n \lambda_{nM}$$

$$\ln \gamma_{-,M} = z_-^2 F + \sum_c m_c \left(2B_{Xc} + ZC_{Xc} \right) + 2 \sum_n m_n \lambda_{nM}$$

This is solved already in the calculation scheme
This should be added to solution model and otherwise to exergy calculations.

From previous we can obtain activity coefficient γ or $\gamma = e^{y}$. Now we can calculate the activity a for the substance as we know the amount fraction x from the stream composition and activity coefficient from the previous:

$$a_i = \gamma_i x_i$$

Gibbs free energy of mixing can be calculated by using chemical potentials and activities:

$$G_i = \sum_i \mu_i^0 + RT ln a_i$$

As for entropy we have:

$S = \frac{H-G}{T}$

It is easy to solve S as we have H from database already in the existing HSC as well as the T of the stream.

The total chemical exergy of the solution becomes:

$$B = \sum_i n_i B_{CH,i} + RT_0 \sum_i ln a_i$$

Where n=amount in moles, T_0 =298.15 and R= gas constant

$$B_{CH,i} = \Delta_f G^0 + \sum_{el} n_{el} B^0_{ch,el}$$

(solved previously in exergy calculations as chemical exergy)

Where $\Delta_f G^0$ = gibbs energy for the formation, n_{el} =amount of element in 1 mol of substance, $B^0_{ch,el}$ =elemental exergy from the table.